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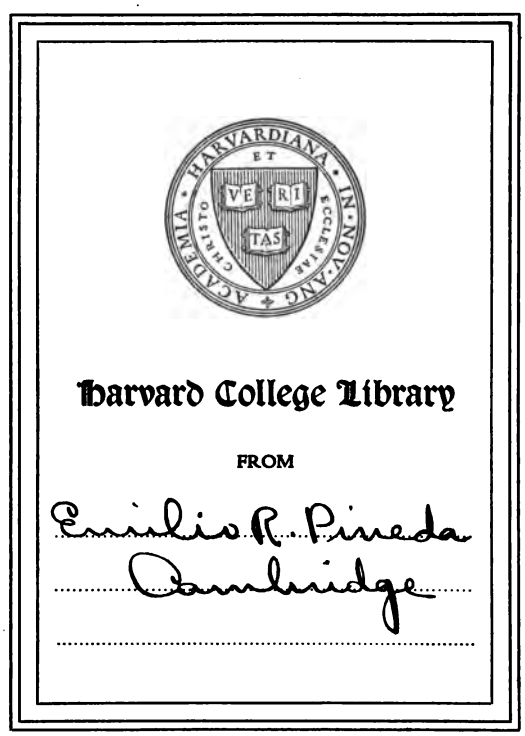

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QUANTITATIVE ANALYSIS

FOR

MINING ENGINEERS

BY

EDMUND H. MILLER, PH.D.

PROFESSOR OF ANALYTICAL CHEMISTRY AND ASSAYING IN COLUMBIA UNIVERSITY

SECOND EDITION, REVISED

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PREFACE TO FIRST EDITION.

This small book on quantitative analysis consists entirely of a series of articles which appeared in the SCHOOL OF MINES QUARTERLY, Volume XXV. It was written primarily, to furnish the engineering students at Columbia University, particularly the mining engineers, with the directions required for their course in quantitative analysis. Also, as so many men now enter the mining course with advanced standing from other universities, colleges and schools, it seemed advisable to show in this way what we require from our mining students in quantitative work.

No attempt is made to cover the entire field of inorganic analysis; but a few important analyses are given in considerable detail; the aim being to describe these analyses with enough explanation for the student to work understandingly and with an appreciation of the modern theories of chemistry. References will be found at the end of the chapters to books and articles giving additional information on the subjects treated; and the last chapter is devoted entirely to references on important analyses which are not given in the text nor required in the course for mining engineers.

In describing some well-known methods, it is not always possible to give to each chemist exactly the credit he deserves in its development, so acknowledgment is made here to all the standard books on the subject, and special references are made to the more recent journal articles. The methods as described in many cases embody the results of investigations, which have been carried out in the Havemeyer laboratories by the recent graduates in chemistry. Acknowledgment is made to this work and also to Dr. Morgan, Dr. Sherman and Dr. Joüet for helpful suggestions and corrections. E. H. M.

QUANTITATIVE LABORATORY,
COLUMBIA UNIVERSITY, Dec. 31, 1903.

PREFACE TO SECOND EDITION.

In this second edition only such changes have been made as were indicated to his colleagues by the late Professor Miller, or were necessary in order to bring the subject matter and references down to date. H. C. SHERMAN.

COLUMBIA UNIVERSITY,
June, 1907.

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CHAPTER I.

Ionization.

Chemistry to-day must consider, besides atoms and molecules, ions. Ion was the name given by Faraday to the moving particles in a solution which carried the electric current. Many years later, in 1887, Arrhenius, in attempting to explain the abnormally high osmotic pressures given by many aqueous solutions, discovered that only those solutions which conducted the current gave these high osmotic pressures, and so decided that there were present in such solutions particles other than molecules, which he designated by Faraday's name of ions.

Although there is now abundant evidence of the existence of ions, a few words on osmotic pressure may not be out of place, as it affords one of the most convincing proofs of ionization. It has been shown by experiment that the laws of gases in regard to pressure and temperature apply equally to substances in solution. Here the volume is the volume of the solution, and the pressure is not exerted, as in the case of gases, on the walls of the containing vessel; but requires for its detection a semi-permeable membrane of such a nature that the solvent can pass through, but the dissolved substance can not. Such diaphragms were made by Pfeffer in 1877, and with them he showed that the osmotic pressure of such substances as sugar obeyed the gas laws; that doubling the number of molecules of sugar, dissolved in a given volume of water, doubled the osmotic pressure, and also that increasing the temperature increased the pressure in the same ratio as for gaseous molecules.

This important agreement having been shown for a number of substances, usually organic, it was found that there were many salts and other inorganic compounds, such as acids and bases, which did

not obey the law, but which gave osmotic pressures greater than those calculated from the number of molecules present, so that, as the pressure depended on the number of particles, there must be more particles than molecules present. This gave rise to the theory of ionization or electrolytic dissociation which is: that many compounds, such as salts, when they are dissolved in water are dissociated into ions, and that these smaller particles conduct the electric current and are the active elements in most chemical reactions. When a simple salt dissolves in water, such as sodium chloride, two ions are formed, $\overset{+}{\mathrm{Na}}$ and $\bar{\mathrm{Cl}}$; in this case the ions coincide in chemical formula with the atoms, but they differ chemically. If we place the metal sodium, with which we are familiar, in water, an immediate reaction results with the evolution of hydrogen and the formation of caustic soda; and also the familiar chlorine is a gas of disagreeable odor and active properties, which differs entirely from the chlorine ion. The difference between these elements in the ordinary and in the ionic condition is one of electric charge.

The ions do not always coincide with the atoms, however; when cupric sulphate is dissolved in water we have $\overset{+\,+}{\mathrm{Cu}}$ and $\bar{\mathrm{S}}\bar{\mathrm{O}}_4$ ions, the solution being blue on account of the presence of the $\overset{+\,+}{\mathrm{Cu}}$ ions; if a current of electricity is passed through such a solution the copper ions travel to the cathode; and as the positive charges of electricity they carry are neutralized by the negative current, the blue copper ions are converted to the red metallic copper which deposits on the cathode.

The electric charge carried by the equivalent weight in grams of any element or radicle is 96,540 coulombs, so to liberate one gram of hydrogen by the electrolysis of water we must supply 96,540 coulombs of electricity. As in cupric sulphate, copper is a diatomic element, the hydrogen equivalent is one half the atomic weight, so that 96,540 coulombs will deposit 31.8 grams; or we may say that the cupric ion carries a double charge of electricity. This is designated $\overset{+\,+}{\mathrm{Cu}}$, to show two positive charges. The importance of this quantity of electric charge, not only from the theoretical, but also from the practical standpoint, is seen when we consider solutions of an element in two degrees of oxidation or where the ion has different degrees of valence or of electric charge. Take, for example, solutions of cuprous and of cupric salts, with the cuprous

there is but a single charge of electricity, with the cupric a double; so 96,540 coulombs will deposit from a cuprous solution of 63.6 grams of copper and from a cupric 31.8: or if we consider the amperage, the same current will in the same time deposit twice the copper from a cuprous that it will from a cupric solution.

This shows the intimate connection which exists between the valence of an ion and its electric charge. It is accompanied often by marked physical differences.

Compare solutions of potassium manganate * and potassium permanganate, one green the other purple, but both composed of the same ions, K and MnO_4. The only difference is that with the manganate we have $\dot{K}$, $\dot{K}$ and $\bar{M}n\bar{O}_4$, while with the permanganate $\dot{K}$ and $\bar{M}nO_4$, the anion or negative ion has a double charge in the manganate. Similarly there is a difference between the colors of ferrous chloride and of ferric chloride depending on whether the Fe ion has two or three positive charges.

The following list † gives the most important cations and anions:

CATIONS.

Monovalent. — H in acids, K, Na, Li, Cs, Rb, Tl, Ag, NH_4, Cu (cuprous), Hg (mercurous).

Divalent. — Ca, Sr, Ba, Mg, Fe (ferrous), Cu (cupric), Pb, Hg (mercuric), Co, Ni, Zn, Cd.

Trivalent. — Al, Bi, Sb, Fe (ferric).

Tetravalent. — Sn, Zr.

ANIONS.

Monovalent. — OH in bases, F, Cl, Br, I, NO_3, ClO_3, ClO_4, BrO_4, MnO_4 (permanganates) and the anions of all other monobasic acids, *i. e.*, the acid molecule minus one hydrogen which goes to the kathode.

Divalent. — S, Se, Te, SO_4, SeO_4, MnO_4 (manganates) and the anions of dibasic acids.

Tri- to Hexavalent. — The anions of tri- to hexavalent acids. Elementary anions with a valence of more than two are not known.

* Add a little alkali to prevent rapid decomposition.

† Taken from Ostwald's Scientific Foundations of Analytical Chemistry.

The degree of ionization is measured most readily by finding the electrical conductivity of the solution, for this is dependent on the number of ions present and the rate at which they move; and is more convenient than obtaining the results from the osmotic pressure, on account of the difficulty in making diaphragms which shall resist these enormous pressures and at the same time not let through any of the dissolved substance. In this way it is shown that most organic compounds are practically undissociated into ions.

It is true that organic acids and bases are dissociated in aqueous solution, but the great majority of the important organic compounds, such as alcohols, ethers, carbohydrates, hydrocarbons, etc., are practically without appreciable ionization.

The extent of the ionization of some of the typical inorganic compounds is as follows: In a tenth normal solution most simple salts such as potassium sulphate, sodium nitrate, potassium chloride, ammonium chloride and so on, are almost completely dissociated. There are but few exceptions to this statement; one is the salts of cadmium and another those of mercury, the most important being mercuric chloride, and the fact that the nitrate gives many reactions which are not obtained from the chloride, may be explained by the inertness of the chloride, due to lack of dissociation into ions. With acids the dissociation is into hydrogen ions and negative ions consisting of the negative element or radicle as $\dot{H}$, $\bar{Cl}$; $\dot{H}$, $\bar{N}O_3$; $\dot{H}$, $C_2\bar{H}_3O_2$; $\dot{H}$, $\dot{H}$, $\bar{S}\bar{O}_4$; $\dot{H}$, $\dot{H}$, $\bar{C}_2\bar{O}_4$, etc. The concentration of the hydrogen ions measures the strength of the acid. In a tenth normal solution the percentage of ionization is as follows: Hydrochloric acid, 99.5 per cent.; nitric acid, 100 per cent.; sulphuric acid, 69 per cent.; acetic acid, 1.4 per cent.; carbonic acid, 0.174 per cent.; sulphydric acid (H_2S), 0.075 per cent.; boric acid, 0.013 per cent. These values give definite expression to the ideas concerning the relative strength of acids though they contradict some of the old views: for instance, it has been often stated that sulphuric acid is the strongest, because it will displace other acids from their salts, but it is less ionized than hydrochloric acid, and the fact that when evaporated with sulphuric acid, chlorides are changed to sulphates, is explained by the easy volatility of hydrochloric acid and is not a proof that sulphuric is the stronger acid.

Similarly the strength of a base depends on the concentration of the OH ions. At a dilution of tenth normal, potassium hydroxide is 100 per cent. dissociated, sodium hydroxide, 95.3 per cent. and ammonium hydroxide only 1.6 per cent. So that nitric and hydrochloric acids bear almost the same relation to acetic acid as the fixed caustic alkalies do to ammonia.

Ionization increases with dilution to a very marked degree so that at an infinite dilution all ionizable substances are completely dissociated. The effect of dilution is shown by the following values for monochloracetic acid: $N/2$, 5.4 per cent. dissociated; $N/8$, 10.57 per cent.; $N/32$, 20 per cent.

Temperature has but little effect on the degree of ionization, but a very considerable influence on the rapidity with which the ions travel; so that rise in temperature increases the conductivity of the solution as it increases the rate of migration of the ions, and therefore must be considered in calculating the ionization from the conductivity.

So far water alone has been considered as the solvent, as it has the greatest dissociating power; in other solutions the degree of ionization is much less; but water itself, although usually considered a non-conductor, is dissociated very slightly, and is found to contain one gram of hydrogen ions to twelve million liters. As will be explained later even this infinitesimal ionization makes water a reagent of importance in a number of quantitative reactions.

The reaction in neutralizing sodium hydroxide by hydrochloric acid is usually written: $NaOH + HCl = NaCl + H_2O$.

This represents the weights which take part in the reaction and if we evaporate off the water, the calculated quantity of sodium chloride will be obtained. But while in solution these substances are not all present as molecules, and if we perform the neutralization with solutions more dilute than tenth normal, so that the ionization of the acid, alkali and salt is practically complete, we shall have:

$$\dot{Na}|\bar{O}H + \dot{H}|\bar{Cl} = \dot{Na}|\bar{Cl} + H_2O$$

or on both sides of the equation we have Na and Cl ions, but instead of H ions and OH ions we have undissociated water. So that the essential part of this and every other reaction of neutralization is the formation of water. This is strikingly confirmed by

the fact that the heat of neutralization of equivalent quantities of caustic alkali by different strong acids is the same, 13,700 calories for the equivalent weights in grams.

The following may emphasize the importance of considering what is present in a solution instead of what was dissolved to produce it: Suppose the formula weight in milligrams of potassium chloride and the formula weight in milligrams of sodium nitrate are dissolved together in a large volume of water so that the dissociation is complete; and that in another vessel in an equally large volume of water, the formula weights in milligrams of potassium nitrate and of sodium chloride are dissolved. The two solutions are identical for there are present in each the same number of the same four ions $\dot{N}a$, $\dot{K}$, $\bar{C}l$ and $\bar{N}O_3$.

The characteristic colors of solutions are due either to the color of the ion or the color of the molecule. When solutions of nickel or copper are evaporated to fumes with sulphuric acid, they lose their characteristic colors, for when the water has been removed there is no longer ionization — or color. Cobalt chloride dissolved in alcohol is blue, the color of the molecule; when water is added it becomes pink, showing the color of the ion. In the same way cupric chloride changes from brown to blue. The change in the colors of indicators is due to the passing from an ionized salt of the indicator to an undissociated molecule.

While it is not claimed that there is no reaction without ionization, it is certain that in the case of aqueous solutions of inorganic compounds we are dealing with ionic reactions. In qualitative analysis most of the tests are tests for ions, as silver nitrate for the chlorine ion; but if sodium chlorate is dissolved in water and silver nitrate is added, no precipitate of silver chloride is produced; for though there is chlorine present there are no chlorine ions, as the dissociation is into Na and ClO_3. Also with a solution of sodium chlorplatinate there is no production of silver chloride but a yellow precipitate of silver chlorplatinate is formed, a test for the $PtCl_6$ ion.

When ammonia is added to a solution of ferric chloride or any other solution containing ferric ions, ferric hydroxide is formed; but no such reaction takes place when it is added to a solution of potassium ferricyanide, although it contains iron in the ferric con-

dition, for the ionization is into K ions and $Fe(CN)_6$ ions. If a test for the $Fe(CN)_6$ ion is applied in each case, for example ferrous ions, nothing results with the ferric solution; while with the ferricyanide a characteristic precipitate is formed, Turnbull's blue.

As inorganic qualitative analysis is made up largely of such tests and separations, there is no lack of further illustrations of the application of the theory of ionization to this important branch of analytical chemistry.

CHAPTER II.

Mass Action.

In order to understand the most important effects of ionization on quantitative analysis, the law of mass action must be considered in an elementary way. This will be done by taking it up first in connection with molecular and then with ionic dissociation.

Dissociation was the name given originally by Deville to the separation of a molecule into smaller molecules by heat. For instance, when hydriodic acid gas is heated above 180° C. it begins to separate into hydrogen and iodine. This decomposition increases as the temperature is raised still further and decreases on lowering the temperature again, so that for hydriodic acid the amount of dissociation is always the same at a given temperature and pressure. This is often expressed as follows: $2HI \rightleftharpoons H_2 + I_2$ which shows that the reaction may go from right to left or from left to right depending on conditions. Ammonium chloride dissociates readily into ammonia and hydrochloric acid gases, so that when this process is complete, there will be present double the number of molecules and, according to Avogadro's law, double the pressure if the volume is unchanged. This is a disturbing feature in those methods of molecular weight determination which rely on vapor density determinations, for the molecular weight decreases with increasing dissociation as the temperature rises. With sulphur the molecular weight at low temperatures shows eight atoms in the molecule, while at 860° C. there are only S_2 molecules present. Ferric chloride gives values agreeing with the formula Fe_2Cl_6 at 320–440° but dissociates at higher temperatures. Nitric oxide is a mixture of NO_2 and N_2O_4, at ordinary temperatures, but if the temperature is raised the density diminishes until at 150° it remains constant at 22.9 compared to H_2 as unity, which agrees closely with the calculated weight for NO_2.

In all such cases there is for each condition of temperature and pressure a definite state of equilibrium at which the proportion of the two gases is constant. If "reaction velocity" is considered as

the rate at which this condition is approached, then the state of equilibrium will be that in which the reaction velocities are equal. In the reaction $N_2O_4 \rightleftarrows 2NO_2$. When the state of equilibrium is reached, just as much N_2O_4 is formed in each second by the combination of NO_2 as is dissociated into NO_2. While there is reaction going on, as the two changes are equal in amount and opposite in direction, the effect is nothing and a condition of equilibrium exists. The principle that the reaction velocity at any moment is proportional to the masses of the substances then present, is called the law of mass action.

Guldberg and Waage found that the rate of chemical action (reaction velocity) was proportional to the active mass of each of the reacting substances; that is, to the number of gram molecules or formula weights per liter, whether as a gas or in solution. The following instances illustrate how important the influence of mass is in some familiar reversible reactions: $CaCO_3 \rightleftarrows CaO + CO_2$. At high temperature we have the condition of equilibrium disturbed, dissociation increases and if the active mass of carbon dioxide is decreased by removing the gas the tendency for the reverse reaction is checked and the reaction soon proceeds completely from left to right. On the other hand, when carbon dioxide is passed over cold lime the reverse reaction takes place.

When steam is passed over red-hot iron an oxide of iron is formed and hydrogen; while if the oxide is heated in a current of hydrogen aqueous vapor and metallic iron are produced. The action is reversible, depending on the active mass of the substances present; in the first case there can be no concentration of the hydrogen as it is constantly displaced by fresh quantities of steam; while in the second case the concentration of the steam is prevented by the current of hydrogen.

In accordance with this law, if to a dissociated substance one or more of the products of dissociation is added, the degree of dissociation is diminished, because the active mass is increased and the tendency to the reverse reaction strengthened. When phosphorus pentachloride is vaporized, it is very largely dissociated into phosphorus trichloride and chlorine, but if vaporized in an atmosphere of chlorine, this is prevented by the mass action of the chlorine and the molecular weight is found to correspond very

nearly to that calculated for phosphorus pentachloride, instead of to about half that value.

These principles have a most important bearing on analytical chemistry: for instance, lead can be precipitated as sulphide, from a solution very slightly acid with hydrochloric acid; while on the other hand lead sulphide, whether natural or artificial, can be dissolved readily in strong hydrochloric acid. This is evidently a reversible reaction.

$$PbS + 2HCl \rightleftharpoons H_2S + PbCl_2.$$

In order to have it proceed from left to right, the active mass of the hydrochloric acid must be large and that of the hydrogen sulphide small. This is accomplished by using a considerable quantity of strong acid and allowing the hydrogen sulphide to escape from an open vessel, or better by heating. To get the reverse reaction the concentration of the acid must be reduced by neutralization or dilution, and that of the hydrogen sulphide increased by passing a steady stream of the gas through the solution. If the lead is to be precipitated completely the conditions must be such that the direct reaction is entirely prevented, *i. e.*, there must be very little acid present. The same considerations apply to other sulphides, such as that of cadmium, and to other precipitates as well.

Effects of Mass Action on Ionization.

Just as the laws of gases have been found to apply to ions in solution as well as to gaseous molecules, as is shown by the osmotic pressures of electrolytes, so the law of mass action is found to apply to the ions in solution; and the effect of mass is the same, whether the dissociation is like that of gases into smaller molecules or in solution of an electrolytic nature into ions.

The addition of an ion in common drives back the dissociation. An illustration of this is found in the fact that while aluminum hydroxide is perceptibly soluble in an excess of ammonia, this solubility is diminished by the presence of ammonium chloride or other ammonium salt. As ammonium hydroxide is slightly dissociated and ammonium chloride almost completely, the mass action of the increased ammonium ion drives back the dissociation of the ammonia, and so readily diminishes the concentration of the

hydroxyl ions to such an extent that it is too weak an alkali to dissolve aluminum hydroxide.

The weakening of acetic acid by the addition of an acetate, or the driving back of the dissociation by the addition of an ion in common, can be very strikingly shown by the following experiment: If to a solution of ferric acetate, slightly acid with acetic acid, hydrogen sulphide water is added, no black precipitate is found, but only a separation of sulphur due to the reduction of the iron; but if to another portion of the same solution a considerable quantity of sodium acetate is added and then hydrogen sulphide water as before, a heavy black precipitate of ferrous sulphide will form immediately, because the mass action of the acetions ($C_2H_3O_2$) has driven back the dissociation of the acetic acid to such an extent that it can no longer dissolve iron sulphide.*

To illustrate this action numerically let:

a = the concentration of H ions in gram molecules per liter.

b = the concentration of $C_2H_3O_2$ ions in gram molecules per liter.

c = the concentration of undissociated acetic acid molecules in gram molecules per liter.

k = a constant.

The law of mass action states that the product of the concentrations of the ionized portion equals that of the undissociated portion times a constant, which is dependent on the nature of the substance, the temperature and the pressure; or using the letters to designate these concentrations $ab = kc$. With acetic acid this would mean that the product of the concentrations of the hydrogen ions and the acetions equalled the concentration of the molecules of acetic acid times k.

Let us suppose that there is present 1 gram molecule of acetic acid in 1 liter of water, *i. e.*, 60 grams of actual acetic acid per liter. We shall have a dissociation here equal to 0.42 per cent., *i. e.*, we have present 0.0042 gram molecule of acetions, 0.0042 gram molecule of hydrogen ions, and 0.9958 gram molecule of undissociated acetic acid. Substituting these values for a, b, and c, we get:

* For experiments illustrating ionization, mass action, etc., see an article by A. A. Noyes and Blanchard, *Journal of the American Chemical Society*, **22**, 727, from which some of the experiments described here are taken.

$$0.0042 \times 0.0042 = 0.000018 \times 0.9958,$$

for at 25° C. k for acetic acid is 0.000018.

Now, if 1 gram molecule of sodium acetate is added to this 1 liter of solution, we are adding 0.5 gram molecules of Na ion, 0.5 of acetion, and 0.5 of undissociated sodium acetate, for sodium acetate at this dilution is 50 per cent. ionized. The concentration of the undissociated acetic acid is so nearly that of the total amount present (*i. e.*, 0.9958 instead of 1) that without error we may assume it to be 1. Calling y the concentration of hydrogen ions (*i. e.*, in gram molecules per liter), the formula becomes, if we designate the concentration of hydrogen ions by y,

$$\frac{y \times 0.5}{1} = 0.000018, \text{ or } y = 0.00004.$$

The concentration of hydrogen ions has thus been reduced to about $\frac{1}{100}$ of its previous value (*i. e.*, from 0.0042 to 0.00004 gram molecule per liter) by the presence of 1 gram molecule of sodium acetate of which the dissociation is 50 per cent. Since the strength of a solution of an acid is dependent upon its concentration of hydrogen ions, the presence of one of its neutral salts will always decrease the strength of acid.

This effect, however, is not so great for strong acids as it is for weak ones, for where the acid is largely ionized like hydrochloric acid for example, the effect of its neutral salt is small.

Solubility Product.

The last application of the law of mass action to ions in solution is the case of a saturated solution. When silver is precipitated as chloride in an aqueous solution, although silver chloride is one of the most insoluble precipitates, there is still some remaining in solution; and of this silver chloride in solution, a large percentage is dissociated, so we have again for the dissolved portion, the formula $ab = kc$. Here for each precipitate, kc is a constant at a given temperature, its size depending on the solubility of the precipitate. This value was termed by Nernst the solubility product, and here, as in the case of an unsaturated solution, we have a state of equilibrium only when $ab = kc$. If ab is less than kc some of the precipitate dissolves. If ab is greater than kc more

separates out. In other words as kc is a constant, the equilibrium is adjusted by increase or decrease of the precipitate, instead of by a change in the number of undissociated molecules in solution. Or, the molecules may be regarded as first forming in solution when an ion in common is added; and then, as it is in contact with the precipitate, it can not remain supersaturated and so more precipitate separates out.

So, if to a solution containing a precipitate of silver chloride, an excess of silver nitrate is added, the concentration of the silver ions is increased, the solubility product is exceeded, and silver chloride separates out until ab again equals kc. In this way the addition of ten times the silver ions present reduces the chlorine ions to about one tenth.

This is the explanation of Mulder's end point in the Gay-Lussac titration method, where a portion of the clear supernatant liquid is withdrawn and to one half silver nitrate is added, to the other sodium chloride; when the opalescence in each is equal the end point is obtained.

This cloudiness obtained with silver chloride must be very slight on account of the insolubility of silver chloride. The effect of adding an ion in common is very strikingly shown with silver acetate which is much more soluble. Place one hundred cubic centimeters of a saturated solution of silver acetate in each of three cylinders; to the first add ten cubic centimeters of $4N$ silver nitrate, to the second ten cubic centimeters of $4N$ sodium acetate, to the third several grams of solid sodium nitrate. With the first and second a beautiful crystalline precipitate appears, due to the exceeding of the solubility product by the addition of either silver or acetions; while with the third no precipitate is formed, which shows that the addition of ions not common to the precipitate is without effect.

It is evident that the more soluble the precipitate, the larger will be the solubility product; consequently, the greater must be the excess of reagent added in order to obtain equally complete precipitation. This has been done by chemists for many years as the result of careful quantitative experiment, but the theory of ionization and Nernst's solubility product afford a satisfactory explanation and show why in precipitates like zinc ammonium phosphate.

a much greater excess of reagent is required than with others like barium sulphate. Another application of the principle of driving back the ionization or practically decreasing the solubility by the addition of an ion in common with the precipitate, is in the washing of precipitates. Lead sulphate is washed with one per cent. sulphuric acid, as it was found that it was less soluble in this than in pure water, now the reason is found in the influence of the SO_4 ions. There are many other instances, washing cadmium-ammonium and other phosphates with water containing ammonium phosphate, calcium oxalate with very dilute ammonium oxalate, etc. The last of the washing solution is removed by a final washing with dilute alcohol in those cases where it can not be volatilized.

Complex Ions.

After having given some of the important applications of ionization and mass action to analytical work it is necessary to give an explanation for the apparent exceptions to the laws.

If to a precipitate of silver cyanide an excess of potassium cyanide is added, or if it is washed with a dilute cyanide solution, instead of obtaining more complete precipitation, the precipitate dissolves. This is due to the formation of a compound, $KAg(CN)_2$, which dissociates into K and $Ag(CN)_2$ ions. A different ion is formed which gives a different set of reactions and we could no more expect the $Ag(CN)_2$ ion to give the reactions of the CN ion than the $PtCl_6$ ion to give those of Cl or the $Fe(CN)_6$ ion those of Fe.

So the apparently abnormal results are caused by a change in the ionization.

During the rest of this article reference will be made to these modern theories only in connection with quantitative precipitations, so for further information the reader must consult the numerous books on physical chemistry among which the following are recommended: Ostwald's Scientific Foundations of Analytical Chemistry, Walker's Introduction to Physical Chemistry, Morgan's Elements of Physical Chemistry.

CHAPTER III.

The Analysis of Magnesium Sulphate and the Determination of Alumina in Alum.

CRYSTALLIZED MAGNESIUM SULPHATE.

When the sample is first received it should be examined to find out whether the crystals have effloresced. If they appear uniform and show no white at the edges, the sample is probably homogeneous and contains the full seven molecules of water of crystallization. If there is any evidence of loss of water the entire sample should be thoroughly mixed and about five grams ground up in an agate or porcelain mortar as quickly as possible and immediately transferred to a small specimen tube which is kept tightly stoppered. When a portion is desired for analysis, weigh the specimen tube containing the average sample; then shake out about a gram into a beaker, taking care that all of the powder removed gets into the beaker, stopper and reweigh the tube. The difference between the weights gives the amount taken for analysis. This is termed weighing by difference.

DETERMINATION OF WATER.

Heat a perfectly clean porcelain crucible and cover over a Bunsen burner until all the moisture is expelled, allow it to cool partially and then place it in a desiccator; cover tightly and allow the cooling to continue in this dry atmosphere till the temperature of the balance room is reached. Then weigh the crucible with its cover and record the weight in a note-book at once. Next shake about a gram of the salt from the specimen tube into the crucible and reweigh the tube. Then weigh the crucible with the salt to see whether the weight checks the sum of the weights of the crucible and the sample taken. There may be a slight loss of water during the operation so that the check is satisfactory when the second weight is either the same as the sum of the two or less by two or three tenths of a milligram. Place the crucible on a pipestem triangle with the cover on and heat it for half an hour with

about a four-inch flame from a Bunsen burner, then allow to cool partly, place in a desiccator and when cold weigh quickly. Heat again for ten minutes at the same temperature, cool and reweigh. If all the water of crystallization has been driven off by the first heating the two weights will be identical. If they differ by more than two tenths of a milligram, the heating must be continued till a constant weight is obtained. Should the weight continue to decrease, even after heating for an hour, loss of sulphuric anhydride, SO_3, is indicated and the determination must be repeated at a lower temperature. The ignition should be made at a moderate red heat, between dull and bright red. With a blast lamp all of the sulphuric anhydride can be driven off. A porcelain crucible is recommended for this determination as it is less likely to be overheated than platinum, because it is a much poorer conductor. A comparison of magnesium sulphate with the other alkaline earth sulphates shows a regular increase of stability with the increase of the atomic weight of the metal.

If the contents of the crucible were allowed to stand in the air, moisture would be reabsorbed with an increase in weight.

From the loss in weight the percentage of water is calculated.

Determination of Sulphuric Anhydride.

Weigh out, by difference, into a No. 2 beaker about one gram of the salt (the exact weight being recorded), add about 150 c.c. of hot water and 2–3 c.c. of dilute hydrochloric acid, cover with a watch glass and heat to boiling; while boiling add drop by drop from a pipette 20–25 c.c. of a ten per cent. solution of barium chloride, or else dilute 20–25 c.c. of barium chloride solution with water to about 50 c.c., heat to boiling and then add it to the boiling solution of magnesium sulphate. Boil for at least five minutes, while stirring with a thin glass rod to avoid bumping, then allow to settle. If the precipitate does not settle quickly and completely, boil again for several minutes or heat just below boiling for a longer time. Pour the clear supernatant liquid through a nine-centimeter "ashless" filter, which has been moistened with hot water, allowing the precipitate to remain as far as possible in the beaker. Test a few drops of the filtrate in a watch glass or small test-tube with dilute sulphuric acid to make sure that an

excess of barium chloride is present. Add 100 c.c. of hot water and one c.c. of dilute hydrochloric acid to the precipitate in the beaker; stir well and then allow the precipitate to settle; pour the liquid through the filter and wash the precipitate twice more by decantation with hot water alone. Transfer the precipitate to the filter with hot water from a wash bottle, using a rubber-tipped glass rod to detach any particles which adhere to the beaker, and continue the washing with hot water on the paper till the washings show no test for chlorides, when at least three cubic centimeters are tested with silver nitrate solution, or until three cubic centimeters leave no residue when evaporated in platinum.

Place the filter containing the precipitate, either moist or dry, in a clean, weighed platinum crucible; put this on its side on a platinum or pipe-stem triangle with the cover in front, so that a current of air shall pass in and over the filter. Then heat the cover by a Bunsen burner so that heat shall be reflected into the crucible and the precipitate dried from the top down. When the water is all expelled, heat the crucible itself gently so as to drive out the volatile matter from the paper without allowing it to take fire. When this is expelled place the flame directly under the bottom of the crucible and heat, using a large flame, until all the carbon is oxidized. Allow the crucible to cool, and moisten the contents with concentrated nitric acid and reheat till all the acid is expelled. This must be done gradually and cautiously to avoid loss by spattering, and with the crucible vertical and the cover on tight. The object is two-fold, to oxidize any carbon which may remain and to convert any barium sulphide, reduced by the carbon of the paper, to sulphate (this can also be done by dilute sulphuric acid). Cool and weigh, then retreat with nitric or sulphuric acid, expel the acid and weigh again. The two weights should check; if the second exceeds the first by more than two tenths of a milligram, treat again until a constant weight is obtained.

From the weight of barium sulphate calculate the percentage of sulphuric anhydride.

Properties of Barium Sulphate.

A white and very insoluble precipitate of definite composition. If precipitated in a cold or very dilute solution it usually comes

down in such a finely divided state that it runs through the filter paper unless allowed to stand for several hours. When precipitated in a boiling solution and then heated the particles are larger. The theory of the increase in size is as follows:* The smaller the particle the greater is the ratio of surface to volume; hence the greater proportional contact with the solution. Now every precipitate is soluble to a certain extent, and although this is very small with barium sulphate — about 1 part in 400,000 — still it is perceptible even in the cold and is much increased by heating the solution. When this is done the smallest particles dissolve first, then the solution becomes supersaturated with respect to the larger particles and deposits out barium sulphate on them, so as the boiling continues the larger particles continue to grow at the expense of the smaller. This same action goes on, though very much more slowly, when the precipitate is allowed to stand in contact with the solution in the cold. In order to obtain a successful filtration, this process must proceed till the size of the particles exceeds that of the pores of the filter.

Barium sulphate possesses to a marked degree the property of adsorption, the carrying down of salts from the solution or a sort of condensation of them on its surface; for this reason a very large excess of barium chloride is objectionable, although tending to give more complete precipitation.† The salts carried down in this way do not have their usual solubility and consequently are removed very slowly by washing; so it is always necessary to test the wash-water for chlorides and prove their absence, and not to rely on the fact that a certain volume of water has passed through which would be more than enough to dissolve all of the salts present under ordinary conditions. The other salts likely to be carried down by barium sulphate are alkali and alkaline earth nitrates, chlorides, chlorates and sulphates.

The precipitate is practically insoluble in water, in dilute acetic acid and in hydrochloric acid when present to the extent of one cubic centimeter of dilute acid in one hundred cubic centimeters of water, but it is very appreciably soluble in stronger hydrochloric acid and more soluble in either nitric or sulphuric acid. It is also

* Ostwald, "Scientific Foundations of Analytical Chemistry."

† See solubility product in Chapter II.

soluble to some extent in hot acid solutions containing ammonium chloride, ferric chloride, etc., and in solutions of ammonium acetate, citrates and other organic salts. The tendency of the precipitate to crawl up the sides of the beaker can usually be checked by adding a few drops of hydrochloric acid and boiling.

On ignition barium sulphide may be formed which can be reconverted to barium sulphate according to the reactions:

$$BaS + H_2SO_4 = BaSO_4 + H_2S \text{ or}$$
$$3BaS + 8HNO_3 = 3BaSO_4 + 8NO + 4H_2O.$$

For the precipitation of barium sulphate in the presence of iron see Chapter VII.

Determination of Magnesia.

Weigh out about a gram of the salt by difference into a small beaker; dissolve it in about fifty c.c. of cold water, add five or six c.c. of dilute hydrochloric acid and then make the solution slightly alkaline with ammonia; if a precipitate of magnesium hydroxide forms dissolve this in dilute hydrochloric acid and again make alkaline with ammonia; repeat this, if necessary, till the solution is perfectly clear when alkaline. Next add slowly drop by drop, from a pipette about twenty-five c.c. of a ten per cent. solution of hydro-di-sodium or hydro-di-ammonium phosphate; stir vigorously, avoid touching the sides of the beaker with the stirring rod, and allow to stand in a cool place for an hour; then add a decided excess of ammonia, about thirty c.c. of ammonia water, specific gravity 0.96, and allow to stand in the cold for three hours or longer — over night if convenient.

If the precipitate is perfectly crystalline filter and test a few drops of the filtrate with "magnesia mixture" to make sure that the PO_4 ions are present in excess. It is better to filter and test the filtrate than to withdraw some of the clear liquid with a pipette or tube, as some of the precipitate usually floats. If an excess of the precipitant is present continue the filtration; transfer all of the precipitate to the filter (9 cm.) and wash with very dilute ammonia, one part of strong ammonia water to nine of water (about 2.5 per cent. actual ammonia) till free from chlorides, as shown by no cloudiness being produced when three c.c. of the washings, acidified with nitric acid, are tested with a solution of silver nitrate.

Place a large filter on the top of the funnel to keep out dust, put it in an air-bath and dry at from 115°–120° C. When dry separate the precipitate from the paper over black glazed paper and cover the precipitate with a watch glass; burn the paper, moistened with nitric acid, in a weighed porcelain or platinum crucible until perfectly white, adding more nitric acid if necessary; then add the portion of the precipitate from the paper and ignite, at first gently and then strongly, by the full heat of a burner or with a blast lamp, cool and weigh the magnesium pyrophosphate and calculate the percentage of magnesium.*

Magnesium as well as other phosphates attack platinum in the presence of reducing agents; this is another reason for burning at a low heat and reoxidizing by the addition of nitric acid before heating strongly. Phosphides may be formed even by the reducing gases from the flame penetrating the hot platinum. If the crucible is rough or crystalline after the ignition of a phosphate, it should be scoured with sea sand, as this crystallization gradually penetrates and finally injures the crucible.

Properties of Magnesium Ammonium Phosphate.

Magnesium ammonium phosphate contains six molecules of water of crystallization; it is white and distinctly crystalline; forms slowly when present in small quantity; its separation is accelerated by cold and agitation. If at all flocculent, it is contaminated, most often by magnesium hydroxide or by hydrated silica. The magnesium hydroxide is caused by insufficient ammonium chloride being present to so weaken the ionization of the ammonia that the solubility product of magnesium hydroxide shall no longer be exceeded. This statement is based on recent work † and is accepted by Ostwald in place of the previous theory based on the formation of a complex ion.

If silica is present, it is best to proceed as usual and weigh the magnesium pyrophosphate plus silica; then dissolve out the pyrophosphate by dilute hydrochloric acid, filter and ignite the silica which is insoluble, as it has been dehydrated by the ignition of the precipitate, and deduct the weight from that of impure precipitate.

* For all calculations, the reader is referred to the "Calculations of Analytical Chemistry" by E. H. Miller, which is used as a text-book with these notes.

† Lovén, *Zeits. anorg. Chem.*, 11, 404, 1896.

Magnesium ammonium phosphate is slightly soluble in cold water, one part in 15,000, but very readily soluble in hot water; it is insoluble in dilute ammonia which has an ion in common. If the ammonia is very strong, the precipitate may be too basic, contain more than the right amount of magnesium, hence it is precipitated from a solution which contains but a slight excess of ammonia, to which, after the precipitate has formed, a decided excess of ammonia is added to render the precipitation more complete. In washing, very dilute ammonia should be used as the excess of hydrodisodic phosphate, the usual reagent, is sparingly soluble in strong ammonia. The precipitate is readily soluble in acids. On ignition, the water of crystallization is driven off and also water and ammonia from the molecule giving pyrophosphate.

$$2MgNH_4PO_4.6H_2O + \text{heat} = Mg_2P_2O_7 + 2NH_3 + 13H_2O.$$

It is advisable to dry this particular precipitate before ignition as it retains gases from the paper which leave carbon so intimately mixed with the precipitate that it is very difficult to burn out. The pyrophosphate will stand the heat of a blast lamp without loss. If a loss takes place some other magnesium ammonium phosphate was present and the results are unreliable.

This compound is also used for the determination of phosphoric acid and will be mentioned again under iron ore. In the analysis of crystallized magnesium sulphate the percentages of water, sulphuric anhydride and magnesia should add up to one hundred per cent. whether the sample has lost water or not. Ostwald has recommended calculating the results of analyses to the ions present, for example to Mg and SO_4, instead of to MgO and SO_3, but as the method given here is in general use and is more convenient for metallurgical calculations, the old practice will be adhered to in these notes.

For more information on the phosphates of magnesium see Neubauer, *Journ. Amer. Chem. Soc.*, **16**, 290.

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POTASSIUM ALUM.

Alums are double sulphates of the alkali metals and of a triad metal and contain twenty-four molecules of water of crystallization; for example, $K_2SO_4.Al_2(SO_4)_3.24H_2O$; $Na_2SO_4.Mn_2(SO_4)_3.24H_2O$; $(NH_4)_2SO_4.Cr_2(SO_4)_3.24H_2O$, etc. The formulæ are often divided and written $KAl(SO_4)_2.12H_2O$, etc. There are many other double sulphates which are not alums, for example Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$.

DETERMINATION OF ALUMINA.

Weigh out either by difference or quickly on a watch glass about one gram of potassium alum; transfer it to a No. 2 beaker and dissolve in about 100 c.c. of hot water and five or six c.c. of concentrated hydrochloric acid; make slightly alkaline with ammonia avoiding more than enough to make the solution smell faintly of ammonia while hot. If too much be added, neutralize it by dilute hydrochloric acid. Heat to boiling, while stirring continually to avoid "bumping," and allow the gelatinous precipitate of aluminum hydroxide to settle; decant the clear solution through the filter and wash the precipitate four or five times with 100 c.c. of boiling water, stirring up thoroughly each time and decanting through the filter; transfer to the paper with hot water and wash with hot water till the washings give no test for chlorides or sulphates.

This precipitate is extremely hard to wash on account of its gelatinous nature and must neither be allowed to stand before filtration, as it becomes insoluble and adheres to the beaker, nor should it be allowed to stand over night on the filter unless completely washed, for it contracts on drying, leaving cracks through

which all the wash-water passes, making it impossible to remove the salts by washing.

It is unnecessary to separate this precipitate from the paper and no especial precautions are required to avoid loss in igniting; as the alumina is neither easily reduced nor volatile if the chlorides have been removed. This precipitate should always be ignited for 5 to 10 minutes over a blast lamp. Weigh the alumina and calculate the percentage.

Properties of Aluminum Hydroxide.

Aluminum hydroxide when freshly precipitated is very readily soluble in acids, both strong and weak, but on standing it becomes difficultly soluble even in hydrochloric acid; it is also soluble in caustic alkalies and to a slight extent in ammonia. In the plan just given the solvent action of the slight excess of ammonia is so weakened by the mass-action of the ammonium ions from the ammonium chloride, that it is no longer a sufficiently strong alkali to dissolve aluminum hydroxide. The action of strong alkali in dissolving alumina is to make this very weak base take the part of an acid so that the cation Al''' is changed to an anion $\bar{A}\bar{l}\bar{O}_3$.

A difficulty which may possibly arise is contamination by basic sulphates of aluminum and which may be most readily avoided by pouring the aluminum solution into an excess of ammonia.

The precipitate is in general likely to be contaminated by those metals whose hydroxides are precipitated in a weakly alkaline solution such as iron, manganese, chromium; also magnesium, zinc, cobalt, nickel and copper, also phosphates and arsenates, calcium carbonate and hydrated silica. It is because there are so many possible contaminants, whose separation is difficult, that alumina is often determined by difference; that is, the total weight of the precipitate is taken and deductions made for the impurities from the results of separate determinations.

Organic acids, such as tartaric and citric, and also sugar and glycerin, prevent the precipitation of the hydroxide. The alumina obtained after strong ignition is insoluble in acids, but can be obtained as a readily soluble aluminate by fusing with alkalies, either caustic or carbonate.

For the analysis of bauxite and of aluminum alloys, see Handy,

Journ. Amer. Chem. Soc., **18**, 766, 1896; Phillips and Hancock, *same*, **20**, 207, 1898, and Lunge, "Chemisch-technische Untersuchungs Methoden," Vol. II.

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CHAPTER IV.

Coal Analysis.

SAMPLING.

In all analytical work it is of the utmost importance that the small portion taken for analysis accurately represents the average composition of the lot whose analysis is desired; otherwise the analysis is worthless and misleading for practical purposes. This is especially true with coal, where not only may the sulphur and ash be irregularly distributed, but the amount of moisture may vary from day to day, depending on the weather; if exposed to rain or sunshine the percentage of water differs and for this reason, a carload may have a different composition when it arrives at its destination from that which it possessed when mined. These discordant results should however agree, when calculated to the dry basis if the sampling has been done correctly.

The sample received by the chemist should be at least 5 pounds. This is to be crushed up immediately, so as to avoid any loss of water and quartered, until about a half pound is obtained; this is then ground to 40-mesh and divided in half, and one half immediately sealed as a reserve sample in case of dispute or accident. The remaining sample is weighed and dried at 80°–90° C., allowed to cool in the air, and the amount of moisture determined. It is mixed up thoroughly on glazed paper and quartered down to about twenty grams which are ground fine (100-mesh) and used for the analysis. The object of this treatment is to obtain the water in the sample as received before it has a chance to dry out in the warm atmosphere of a laboratory, and to obtain an air-dried average sample, which is not likely to lose or absorb moisture, from which to weigh out portions for analysis. It is to be borne in mind that water is still present in the coal and that in calculating the analytical results to the original sample the loss in weight in air drying must be considered. This is most readily accomplished, if we regard the original sample as made up of a cer-

tain weight of air-dried sample plus a certain weight of water and correct our percentages accordingly.

These principles apply with equal or even greater force to large lots of ore, matte, slag, etc.

Proximate Analysis.

Moisture. — Dry one gram of the coal in an air-bath in an open porcelain or platinum crucible for one hour at a temperature between 104° and 107° C. Cool in a desiccator and weigh covered. The loss in weight is moisture. This apparently simple determination is very difficult if extraordinary accuracy is required, as water may be lost during the fine grinding of the sample, and also because all the water may not be given off in an hour at the temperature given. It is however the standard method and is sufficiently accurate for technical purposes; the error being probably less than that of sampling. Ash is determined on this portion as indicated below.

Volatile Combustible Matter. — Place one gram of the air-dried sample in a platinum crucible, weighing 20–30 grams, and having a well-fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom 6–8 cm. above the top of the burner. The flame should be 25 cm. high, and the determination made in a place free from draughts. The upper surface of the cover should burn clean but the under surface remain covered with carbon. To find the volatile combustible matter subtract the percentage of moisture from the percentage of loss found here.

This method is evidently arbitrary and open to the objections of the possibility of oxidation on one hand and incomplete expulsion of the volatile matter on the other; but by following it carefully the results possess uniformity, if not scientific accuracy, and it is the method in general use. The loss due to oxidation, particularly with coke, can be diminished by using a much larger sample, say 10 grams. With coke the last of the volatile matter should be removed by a couple of minutes over a blast lamp.

Ash. — Burn the portion of powdered coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, till free from carbon. This sample can be

burned much more quickly than the dense carbon or coke left from the determination of the volatile combustible matter.

Fixed Carbon. — This is found by difference. Either subtract the percentage of ash from the percentage of coke (residue left when water and volatile matter are driven off) or subtract the sum of the other percentages from 100.

Determination of Sulphur.

Sulphur exists in coal in three conditions — as sulphide, FeS_2, as alkaline earth sulphate, $CaSO_4$, and as an organic compound. On heating FeS_2, out of contact with the air, Fe_7S_8 is usually left behind. So in the determination of the volatile combustible matter, the sulphur present as an organic compound (if any) and nearly one half the sulphur present as pyrites is driven off. And in burning off the fixed carbon the Fe_7S_8 is changed to Fe_2O_3 with a loss of the sulphur remaining from the pyrites. The ash contains the sulphate sulphur.

It was formerly customary to consider all the sulphur was present as FeS_2, and that one half of this went off with the volatile matter and the second half with the fixed carbon; so that one half the percentage of sulphur was subtracted from each of these percentages to make the results add up to 100 per cent. Although this method is still in use it is evidently not strictly in accordance with the facts and, as it is never correct to state more in a report than is actually known, it is preferable to report the percentage of sulphur separately and let the sum of the other determinations add up to 100 per cent.

When the sulphur in the ash is desired separately from the total sulphur, a large portion, 10–12 grams, of the coal is burned and the sulphur determined in the ash by methods similar to those which will be given under iron ore and slag analysis.

Total Sulphur. Eschka Method Modified. — One gram of the finely pulverized coal is mixed with one gram of light magnesium oxide and 0.5 gram of anhydrous sodium carbonate in a platinum dish having a capacity of 75–100 c.c. or a Meissen porcelain crucible, and heated with an alcohol lamp. When great accuracy is not required a gas burner may be used, the dish being protected, as far as possible, from the products of combustion, which contain

sulphur. The mixture is stirred frequently with a stout platinum wire or glass rod and the heat applied gradually, especially with soft coals, until strong glowing has ceased; then the heat is increased until in fifteen minutes the bottom of the dish is at a low red heat, which is maintained until all the carbon is burned out. The residue which should be nearly white and porous is transferred to a No. 2 beaker with about 50 c.c. of water, 15 c.c. of bromine water are added and the whole boiled for at least 5 minutes, allowed to settle and decanted through a filter and boiled a second and third time with 30 c.c. of water and then washed very thoroughly with hot water. The filtrate is acidified with hydrochloric acid so as to have an excess of about 1 c.c. and boiled to expel any free bromine. Then to the hot solution barium chloride (10 per cent. solution) is added drop by drop, until 10 c.c. have been added and the solution boiled or heated on a water-bath until the precipitate settles quickly, filtered and treated as already described. From the weight of $BaSO_4$ the percentage of sulphur is calculated.

The treatment with magnesium oxide, sodium carbonate and air, oxidizes the sulphur present to sulphurous and sulphuric anhydrides which combine with the bases present. The mass must not fuse as it would then be much more difficult to oxidize and as the silica from the ash would thereby be rendered soluble. It is for these reasons that magnesia is selected on account of its bulk and infusibility.

When the mass is leached the soluble sulphites and sulphates pass into solution, together with the excess of sodium carbonate, while the bulk of the magnesia and the ash remain insoluble. It is at this point that an important reaction takes place, the ash may contain calcium sulphate which is acted on by the excess of sodium carbonate, giving calcium carbonate which remains behind and sodium sulphate which passes into solution, and by this means the total sulphur is obtained in the filtrate.

The bromine, in the alkaline solution, oxidizes any sulphites present to sulphates. It is important to acidify after, not before filtering, as the latter would take magnesia into solution; also alkaline earth carbonates which would immediately react, giving insoluble sulphates and so cause low results.

The solution after filtration is made but slightly acid and a

liberal excess of barium chloride is added to get complete precipitation of all the sulphur as barium sulphate.

This method is most satisfactory, but for very accurate results certain precautions not already mentioned must be observed:

The magnesia and the sodium carbonate must be tested for sulphur as they often contain small quantities which are enough to interfere with the accuracy of the determination. If present the sulphur should be determined in 20-gram lots and the percentage marked on the reagent bottles and deducted from the results.

The residue after leaching may in some cases contain sulphur, if much calcium sulphate should be present and the excess of sodium carbonate be insufficient to convert it. In such a case the residue is treated with hydrochloric acid and filtered, the filtrate neutralized closely and any sulphate precipitated as barium sulphate and added to that obtained in the main portion.

The original barium sulphate may be contaminated by silica. If the heat has been too high or the ash very siliceous, some sodium silicate may be formed and dissolved, and hydrated silica be carried down with the barium sulphate. To avoid this, evaporate the solution to dryness after the bromine is boiled out and heat at 120° C. until the hydrochloric acid is driven off to render the silica insoluble; then take up with hydrochloric acid and water, filter and determine the sulphur as usual in the filtrate.

For further information see Report to American Chemical Society, *Jour. Amer. Chem. Soc.*, **21**, 1119, 1899, Stoddart on the determination of sulphur in coal, *same*, **24**, 852, 1902, and Somermeier, on moisture in coal, *same*, **28**, 1630, 1906.

CHAPTER V.

Ferric Ammonium Alum.

DETERMINATION OF FERRIC OXIDE GRAVIMETRICALLY.

By Precipitation with Ammonia. — Dissolve about a gram of the alum in hot water and a few c.c. of hydrochloric acid, heat to boiling and add at once, but carefully to avoid spattering, an excess of ammonia; heat till the precipitate collects well; decant through a filter and wash by decantation and then on the filter with hot water, till free from chlorides. Transfer the paper and precipitate to a weighed platinum crucible and moisten with strong nitric acid; ignite gently till the water and volatile matter have been expelled; then allow to cool, moisten again with nitric acid and burn out the carbon; ignite and weigh; check by moistening once more with nitric acid and reweighing; calculate the percentage of Fe_2O_3.

In this particular analysis, the only difficulty is in avoiding any reduction of the ferric oxide by the paper, for if once reduced to the magnetic oxide, complete reoxidation is impossible.* In general, however, when iron is precipitated by ammonia certain precautions must be observed.

The iron must all be in the ferric condition as ferrous iron is not completely precipitated by ammonia, but a white precipitate of ferrous hydroxide is formed which immediately turns green; with mixtures of ferrous and ferric iron, green, black or brownish precipitates are formed.

When the higher groups have been previously removed by hydrogen sulphide, the iron is conveniently reoxidized by nitric acid or hydrogen peroxide.

In the alum we did not boil out the excess of ammonia, but if there are present elements of the fifth periodic group, phosphorus, arsenic, vanadium, etc., the excess of ammonia must be expelled in order to obtain complete precipitation of the iron. Under these conditions phosphorus, vanadium, arsenic and antimony are carried down as well, in combination with the iron as $FePO_4$, etc.

* Hillebrand: U. S. Geological Survey, Bul. 305, p. 59.

Should we wish to use the filtrate for the determination of sulphur, we must proceed differently, as there is danger that the ferric hydroxide may be contaminated by a basic ferric sulphate; although this would not cause any inaccuracy in the iron determination, as the sulphuric anhydride would be driven off on strong ignition. In this case pour the acid ferric solution into a large beaker containing 200 c.c. of water and an excess of ammonia over that required to neutralize the acid and precipitate the iron present. In this way the ammonia will always be in excess and the danger of forming basic sulphates near the neutral point is avoided.

The presence of ammonium chloride, or other ammonium salts, favors the separation of the hydroxide and prevents its becoming colloidal. They must be washed out, however, to prevent loss of ferric chloride on ignition. Ferric hydroxide is soluble in acids both weak and strong, and insoluble in alkalies. Its precipitation is prevented by citric acid, tartaric acid and other organic substances such as sugar, glycerine, etc., because they form complex ions containing Fe, which no longer give the reaction of the ferric ion.

This precipitate is very likely to be contaminated not only by sulphates, phosphates, arsenates, etc., as already mentioned, but also by hydrated silica and by the hydroxides of aluminum, chromium, manganese, and also by those of magnesium, cobalt, nickel, zinc and copper. Of the latter, magnesium and zinc can be removed by reprecipitation, but with copper, nickel and cobalt the separation is not easy. As these elements, or some of them, are always present in iron ores, the gravimetric method is seldom used except to throw down together hydroxides of aluminum and iron with phosphoric acid.

One other property of ferric salts should be mentioned, the effect of water on them. Ferric iron is a very weak base and when combined with a weak acid in a neutral solution it is easily hydrolyzed, especially on heating, with the formation of basic ferric salts. It is for this reason that hydrochloric acid is added to the alum when it is dissolved, to give a clear solution, as well as to form ammonium chloride.

Determination of Ferric Oxide Volumetrically.* By Potassium Permanganate.

A standard solution of potassium permanganate is required which should be approximately $N/10$. Dissolve 6.4 grams of pure potassium permanganate in about 400 c.c. of water, warm slightly to assist the solution, then filter through a layer of asbestos supported by a cone or porcelain plate in a large funnel or a Gooch crucible; allow the solution to run into a clean dry liter flask; wash the residue on the asbestos (hydrated manganese dioxide) with water and then dilute the permanganate solution in the flask to the delivery mark with cold distilled water (if the solution is still warm allow it to cool to the temperature for which the flask was graduated and make up the contraction by more water). Pour the contents into a clean dark glass bottle, with a well-fitting ground-glass stopper; fill the liter flask again with water to the delivery mark and add this also to the bottle containing the permanganate solution. Mix by very thorough shaking and allow to stand several hours before standardizing.

The warming and removal of the dioxide, which is formed by organic dust, etc., by filtration, gives a solution which retains its strength better than if this process goes on gradually in the bottle.

The solution must be filtered through asbestos for it is decomposed by filter paper, rubber and other organic materials. If an old permanganate solution can be obtained, it will remain more constant and so require standardizing less frequently than a freshly made solution. The solution obtained will be nearly $N/10$, but its strength must be determined by experiments, and the results should not differ from each other by more than one in the fifth place; *i. e.*, 0.00561 and 0.00562 is the greatest error allowable in duplicates for the value of 1 c.c. in terms of iron. Many methods of standardizing have been proposed † of which three will be mentioned here.

Iron Wire Method. — Take a spool of soft iron wire, such as is used by florists, and remove any superficial layer of oxide by emery

* For definition of normal solution and general discussion of volumetric analysis see Miller's Calculations of Analytical Chemistry, Chapter VI.

† Thiele and Deckert, *Zeits. angew. Chem.*, 14, 1233, 1901; Dupré and Muller, *Zeits. angew. Chem.*, 15, 1244, 1902; Rust, *Zeits. anal. Chem.*, 41, 606, 1902.

paper; this will then be very close to 99.7 per cent. iron. The actual iron contents can be determined best by finding the percentage of impurities and subtracting it from one hundred per cent. Weigh out two portions of about 0.2 gram each, weighed exactly of course, but not exactly the same weight; place these in two 250 c.c. Erlenmeyer flasks, add a few grams of sodium bicarbonate to each and then about 100 c.c. of dilute sulphuric acid (one part of concentrated acid to five of water) and immediately close each with a rubber stopper, through which passes a bent glass tube reaching to the bottom of a beaker of distilled water. Heat both the flask and the beaker of water till the wire has completely dissolved,* best on a hot plate heated by gas, then turn off the heat and allow the water in the beaker to be drawn back so that it almost fills the Erlenmeyer flask.

The sodium bicarbonate is added so that carbon dioxide shall be liberated by the action of the sulphuric acid which will replace the air in the flask. The water seal prevents any contact with the air during solution so that the iron dissolves according to the reaction $Fe + H_2SO_4 = FeSO_4 + H_2$, entirely to ferrous sulphate, while the hydrogen bubbles up through the water in the beaker. The water in the beaker is heated also to expel the air dissolved in it, so that it shall be free from oxygen when it comes in contact with the ferrous solution.

There is one situation to be guarded against; if attention is not given and the water is not allowed to run over soon after all the iron is dissolved, the water will keep on evaporating from the flask and the sulphuric acid become concentrated; then, when the hot water comes in contact with the concentrated sulphuric acid an explosion ensues which destroys the determination and may be dangerous to the operator. This is easily avoided by preventing the concentration of the acid. While the iron is dissolving get ready a 50 c.c. burette, which has been found to be accurately graduated, fill it with water and allow it to run out to see whether drops adhere to the sides; if they do clean it thoroughly by means of a solution of potassium dichromate in sulphuric acid; rinse out with water and then introduce 10 c.c. of the permanganate solution, shake thoroughly and allow the solution to run out through the

*The action can be hastened by a drop of hydrochlorplatinic acid solution.

stopcock; then repeat this again and again, so that the burette is wet with a solution so nearly the strength of that to be used that no perceptible dilution results when the burette is filled with the permanganate solution.

Fill the burette and adjust to the zero mark, reading the top of the meniscus with this dark solution.

Pour the ferrous sulphate solution into a large beaker, and rinse out the Erlenmeyer flask with cold distilled water, then dilute with cold distilled water to about six hundred c.c. and the solution is ready for titration. Run in the permanganate solution, a few drops at a time, till the pink color disappears slowly, then drop by drop till finally one drop gives a pink tinge to the whole solution, which is slight but perceptible and permanent. Then wait for two minutes for the solution on the sides of the burette to run down and for the pink color to disappear, if the end has not been reached, and read the volume of permanganate used.

Titrate the second portion of iron wire in the same way and compare the results. The reaction is

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

If the solution should turn brown it is a sign that the manganese is not being reduced completely to manganous sulphate and more sulphuric acid must be added at once.

Standardizing by Mohr's Salt.—Here the iron is already in the ferrous condition, and as the molecular weight is large — about seven times that of the iron atom — any error in weighing, etc., is only one seventh of what it would be when metallic iron is used. The disadvantage is the possibility that some water of crystallization has been lost so that the salt is not exactly $(NH_4)_2SO_4.FeSO_4.6H_2O$. Select crystals which have no white appearance at the edges and weigh out quickly two portions of 1–1.5 grams each; place them in large beakers, add water and 10 c.c. of concentrated sulphuric acid, and when the crystals have dissolved, dilute to about 600 c.c., add more sulphuric acid and titrate as already described. Calculate the results and compare them with those obtained with the wire. Some prefer making up a standard solution of the ferrous salt and measuring this out from a second

burette, but separate weighings of different weights are preferable for beginners because if there should be any error in the weight of the salt taken the titration results would check though the standard would be wrong and the error might not be discovered till much later.

Oxalic acid or *oxalates* may be used for standardizing. The reaction is

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O,$$

which takes place best in a warm solution acid with sulphuric acid. The temperature should be 50°–60° C., and ten grams of manganous sulphate should be added to make the reaction take place rapidly; the end point is the same permanent pink, but, as the oxidation is less prompt than with iron, some time must be allowed, several minutes, to oxidize the last traces. Here if we weigh out crystallized oxalic acid we have the doubt as to whether it really is $H_2C_2O_4.2H_2O$. If the water of crystallization is right the method is excellent. $(NH_4)_2C_2O_4.H_2O$, $KHC_2O_4.H_2C_2O_4.2H_2O$ are salts frequently used; also lead oxalate, PbC_2O_4, which on account of the high atomic weight of lead and the absence of water of crystallization presents theoretical advantages.

Determination in Ferric Alum.—As the iron in the alum is in the ferric condition it must be reduced before titration. This is done most conveniently by passing the solution, acidified with sulphuric acid, through a Jones reductor. The simplest form of this apparatus consists of a piece of glass tubing about 2 cm. in diameter and at least 40 cm. long, which is widened at the top like a funnel and drawn out at the bottom like the stem of a funnel, so that it will pass easily through the hole in a rubber stopper. A perforated platinum cone or disc of platinum is placed at the bottom of the wider portion and on this a plug of glass wool, about 8 mm. thick, covered by a thin layer of asbestos fiber; then the tube is filled nearly to the top with granulated zinc, 20–30 mesh — that which will pass through a 20-mesh sieve but not through a 30, is the best size.

The zinc is amalgamated as follows:* Dissolve 5 grams of mer-

* Blair, "Chemical Analysis of Iron."

cury in 25 c.c. of nitric acid, 1.2 sp. gr., dilute to 250 c.c. and pour into a large flask; to this add 500 grams of granulated zinc, shake thoroughly for two minutes and then pour off the solution; wash the zinc repeatedly with water and fill the reductor with it.

Weigh out two portions of ferric ammonium alum, about 2 grams each, dissolve these in about 100 c.c. of water, and about 50 c.c. of dilute sulphuric acid (1:5). Place the reductor through the rubber stopper of a stout 600 c.c. Erlenmeyer flask which is connected by a side tube with the suction. Pour the solution into the reductor and turn on the suction gently, adding the rest of the solution so that the zinc is always covered. As the ferric solution passes through, add 200 c.c. of water containing 10 c.c. of concentrated sulphuric acid and then follow this with 100 c. c. of water.

The solution, assuming its volume not to exceed 200 c.c., should require at least four minutes to pass through the reductor. The titration can be made directly in the reductor flask after dilution if necessary, as already described. The duplicates should agree closely and check the gravimetric results when calculated to percentage of Fe_2O_3. (The permanganate standard is in terms of Fe.)

The length of the column of zinc should be at least 35 cm., and when freshly filled or after standing some time it should be washed with dilute sulphuric acid. Then a second lot of dilute sulphuric acid should be run through and this titrated with permanganate. If more than a drop is required to color the solution, the amount must be determined and subtracted from the subsequent titrations. This is due to the iron which is usually present in zinc and whose solution may not have been entirely prevented by the amalgamation.

If air is allowed to pass through the reductor after an acid solution and then followed by acid again, hydrogen peroxide may be formed, which uses up permanganate according to the reaction:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 5O_2 + K_2SO_4 + 2MnSO_4 + 8H_2O,$$

and so gives too high results.

This method can also be applied in standardizing. Dissolve the iron wire by dilute sulphuric acid in a beaker in the presence of air, then run the solution of ferric and ferrous sulphates through the reductor and titrate.

The permanganate titration depends on the oxidation of the iron present from the ferrous to the ferric condition by a solution of known oxidizing power, hence any other oxidizing or reducing agents which would affect permanganate must be absent. Sulphuric is the best acid to use, but hydrochloric is permissible under carefully regulated conditions.

By Potassium Dichromate.

Make up a solution of potassium dichromate containing 4.9 grams per liter and standardize it as follows: Weigh out at least two portions of clean iron wire about 0.2 gram each, and dissolve them in small beakers in about 20 c.c. of hydrochloric acid 1.1 sp. gr.; rinse down the cover and sides of the beaker and while still hot add drop by drop from a pipette a very dilute and strongly acid solution of stannous chloride until the solution becomes colorless; then dilute to about 50 c.c. and add at once 10 c.c. of a saturated solution of mercuric chloride, which should give a white silky precipitate of mercurous chloride; pour this solution into distilled water containing 20 c.c. of concentrated hydrochloric acid and dilute to about 600 c.c. Place on a porcelain tile or plate some drops of a very dilute and freshly prepared solution of potassium ferricyanide. Run in the dichromate solution until nearly the calculated quantity has been added, then after stirring, remove a drop and place it in contact with a drop of ferricyanide on the plate. A blue color will result due to the reaction between the ferricyanide and the ferrous iron still present; continue adding dichromate from the burette until no blue coloration is produced with a drop of the indicator. Treat the second portion in the same way and calculate the standard of the solution in terms of iron. The results should agree as closely as in the permanganate titration. The reaction of titration is:

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2KCl + 2CrCl_3 + 7H_2O$$

and for the blue color,

$$3FeCl_2 + 2K_3Fe(CN)_6 = Fe_3(Fe(CN)_6)_2 + 6KCl.$$

The special precautions to be observed are: To keep the solution concentrated, hot and strongly acid when reducing by stannous chloride and to avoid an excess of more than one drop. If

the solution is cold, dilute or insufficient hydrochloric acid is present, the reduction is slow and an excess of stannous chloride is added before the solution becomes colorless; then when the mercuric chloride is added a black precipitate of finely divided mercury results, which destroys the determination as it is likely to be oxidized by the potassium dichromate.

The reactions are:

$$Fe + 2HCl = FeCl_2 + H_2,$$
$$2FeCl_2 + 2HCl + O \text{ (from the air)} = 2FeCl_3 + H_2O,$$
$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4,$$

and with the excess of stannous chloride,

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2.$$

If the excess of stannous chloride is too great we get

$$SnCl_2 + Hg_2Cl_2 = SnCl_4 + 2Hg.$$

The 10 c.c. of mercuric chloride solution should be added at once to get it in excess as regards the stannous chloride as quickly as possible and so avoid the last reaction. The indicator must be free from ferrocyanide, for if this is present we get a blue with the ferric salt as well, and so no end point. It should for this reason be made up by dissolving a crystal the size of a pin head in water in a small watch glass; if more concentrated, the brown coloration due to ferric ferricyanide may mask the blue. When properly carried out the end point is extremely sensitive.

To determine the iron in the alum, weigh out two portions of about 2 grams each and dissolve in hydrochloric acid (1 : 1), using 30–40 c.c. and heating; then reduce by stannous chloride, using more, of course, than with the wire, and carry out the operation just as in standardizing.

This method has many advantages: first, it is extremely accurate; second, it can be done, and is best done, in a hydrochloric acid solution which is the best solvent for iron in ores; third, the reduction by stannous chloride is very rapid and at the same time does not reduce the titanic chloride often present from magnetites,

while zinc reduces this to $TiCl_3$, which is reoxidized by permanganate giving too high results.

The disadvantage is the outside indicator which is tiresome and may cause inaccuracy when too many drops are removed. It is evident that this solution may be standardized by Mohr's salt but not by oxalic acid or oxalates as there would be no end point.

CHAPTER VI.

Analysis of Iron Ore.

Under this title the complete analysis of all iron ores might be considered, and then the determination of most of the known elements would be involved as they are occasional constituents of iron ores. However as this is not often required of the chemist, only the determinations of greatest technical importance will be given in detail, namely, iron, silica, sulphur and phosphorus. When only a partial analysis is made, the iron is most easily determined in separate portions, while a larger quantity is taken for the determination of silica, sulphur and phosphorus.

Determination of Iron.

By Potassium Dichromate. Penny's Method. — Grind about a gram of the sample in an agate mortar till it feels like flour, from this weigh out two portions of about 0.35 gram each and treat them in small beakers with from one to three c.c. of stannous chloride solution (250 grams per liter), depending on the amount of iron oxide present, and 20 c.c. of hydrochloric acid, 1.1 sp. gr. The beakers should be covered and heated on a hot plate for from ten to fifteen minutes, until the residues are white or until no further solution can be effected. In most cases complete solution of the iron takes place readily if the ore is ground to an impalpable powder but with some ores, particularly magnetites, pyroxene and other insoluble silicates containing iron may be present, which require a fusion with sodium carbonate, etc., to obtain all the iron from the greenish residue.

(*a*) The *residue is white*, the solution may be either colorless or yellow; if it is colorless, an excess of stannous chloride has been added, which must be destroyed by adding potassium permanganate or hydrogen peroxide till the solution becomes yellow, otherwise a black precipitate of mercury would be formed in the next operation. Rinse down the sides of the beaker and the cover and while the solution is still hot add drop by drop a very dilute

solution of stannous chloride until the iron is reduced, then dilute to about 50 c.c. and add 10–12 c.c. of a saturated solution of mercuric chloride as already described, and continue the titration as under iron alum.

(*b*) If the *residue is greenish* filter it off and titrate the soluble iron. Fuse the residue with at least six times its weight of potassium and sodium carbonates* in a platinum crucible for half an hour, using a blast lamp if necessary to obtain a clear fusion; dissolve the melt in hydrochloric acid and water and add an excess of ammonia, filter out the impure ferric hydroxide and wash it twice with hot water; dissolve through the filter by hot dilute hydrochloric acid into a No. 1 beaker, reduce by stannous chloride, add mercuric chloride and titrate as usual by potassium dichromate. Calculate the percentage of iron from the total quantity of dichromate used. It might seem that the hydrochloric acid solution of the fusion could be reduced at once for titration, but there are two objections: First, in the presence of the alkali chlorides, double salts with mercury are formed which are easily reduced, so that a black precipitate of mercury almost invariably results. Second, very often in reducing by stannous chloride the color will become darker instead of lighter. This is due to the formation of platinous chloride from the crucible which gives a very intense color, similar to ferric chloride, but which passes into the filtrate when the iron is precipitated by ammonia.

If a weight of sample exactly fifty times the standard of the solution is taken, twice the number of cubic centimeters used is the percentage of iron without further calculation.

By Potassium Permanganate — Zimmerman-Reinhart Method.† — Treat the ore as for the preceding method up to the point where the silky precipitate of mercurous chloride is obtained, being careful that not more than 15 c.c. of hydrochloric acid (1 : 1) is present. Pour this into 500–600 c.c. of cold water to which 8–10 c.c. of "preventive" solution have been added, and titrate by permanganate as usual, except that the end point is not a pink which lasts for several minutes, but the first tinge of pink which colors the solution and then fades away in a few seconds.

* These are mixed in molecular proportions, as this mixture is more easily fusible than either alone.

† Mixer and Dubois, *Jour. Amer. Chem. Soc.*, 17, 405.

The "preventive" solution is made by dissolving 160 grams of manganous sulphate in 1750 c.c. of water, then adding 330 c.c. of phosphoric acid 1.7 sp. gr. (syrupy) and 320 c.c. of sulphuric acid 1.82 sp. gr.

This is the neatest and most rapid method for the determination of iron in ores and is very accurate when properly carried out.

We saw that if hydrochloric acid is present in considerable quantity, especially in a hot solution, that titration by permanganate was impossible, as the hydrochloric acid was oxidized with the liberation of chlorine; so the amount of hydrochloric acid present must be small, not over 10 c.c. of concentrated acid in a bulk of 500 to 600 c.c., and the solution cold.

The effect of the "preventive" solution is as follows: The manganous sulphate acts as a sort of carrier of oxygen, it is changed to the manganic condition by any chlorine which may be formed and this in turn is reduced by the ferrous salt back to the manganous condition * and so does away with the bad effect of hydrochloric acid when it is present in not too large amount.

The sulphuric and phosphoric acids give acidity and sharpen the end point by giving a colorless solution at the end due to the preponderance of ferric sulphate and phosphate instead of chloride.

It is important to carry out this method exactly as described, even slight variations are usually disastrous; for example, if the preventive solution is added to the ferrous solution in the small beaker, instead of to the water used for dilution or else after dilution, the silky precipitate is decomposed into mercurous sulphate which may then give mercuric sulphate and mercury and so spoil the determination.

When there is an insoluble residue it is treated as described under Penny's method and the solutions combined or else titrated separately.

When a complete analysis of an iron ore is made, it may be more convenient to precipitate the iron together with aluminum hydroxide and phosphoric acid in an aliquot part of the solution. This precipitate can be treated by any of the methods given for the ferric alum or for the ore. If titanium should be present it

* Comparable with the action of the oxides of nitrogen in the manufacture of sulphuric acid

will contaminate the ammonia precipitate and in this case reduction by stannous chloride, sulphurous acid or hydrogen sulphide must be used.

Scheme for the Determination of Silica, Sulphur and Phosphorus in one Portion.

Weigh out 5 grams of the ore ground fine in an agate mortar; heat with 50 c.c. concentrated hydrochloric acid and 7–8 c.c. concentrated nitric acid, to prevent loss of sulphur as hydrogen sulphide, in a beaker for about fifteen minutes; dilute, heat again and filter hot; wash the residue twice with dilute hydrochloric acid. Place the filtrate in a casserole to evaporate on a hot plate or steam bath, with a watch glass over it raised to allow the escape of steam by a glass rod triangle. Burn the paper containing the residue in a platinum crucible, add to it at least six times its weight of mixed carbonates and about 0.2 gram of powdered sodium nitrate; mix thoroughly with a stout platinum wire or dry glass rod, being careful not to lose any, and fuse for half to three quarters of an hour over a Bunsen burner, then for 10–15 minutes over a blast lamp. Allow the melt to cool and remove it from the crucible in a cake if possible. Place this in a small casserole, cover with a clock glass and add very cautiously dilute hydrochloric acid until disintegrated; add the solution of what remains in the crucible dissolved in dilute hydrochloric acid; heat to boiling and boil till everything has dissolved, except possibly some white hydrated silica. There should be no dark or gritty particles left, as these show incomplete decomposition of the ore and require refusion. If the decomposition is complete add this solution to the first solution of the ore (which has been evaporating) and evaporate to dryness; when nearly dry stir so as to form irregular granular masses, which present a large surface and hasten the subsequent dehydration. Place in an air-bath (covered) and heat at 115°–120° C., until no odor of hydrochloric acid is perceptible. If the ore is very siliceous moisten it again with hydrochloric acid and repeat this treatment. Add 15–20 c.c. of concentrated hydrochloric acid and heat to dissolve the basic ferric salts; then dilute with water and heat to boiling; filter out the silica which has been rendered insoluble by dehydration and wash alternately with hot

$Mg_2P_2O_7 \cdot 6H_2O$

dilute hydrochloric acid and cold water, then with water till free from chlorides. Burn the paper containing the silica in a weighed platinum crucible, ignite finally over a blast lamp, cool in a desiccator and weigh. To make sure of the purity of the silica drive it off as silicon fluoride, SiF_4, adding first a few drops of dilute sulphuric acid to hold back any titanic oxide and then adding hydrofluoric acid and warming gently on an asbestos pad, and finally igniting strongly. If any residue is left repeat this treatment till a constant weight is obtained. Loss in weight is silica.

If there should be a residue, it is likely to be alumina, titanic oxide or barium sulphate, with possibly traces of iron, and in the present case can be neglected unless barium sulphate or titanic oxide is present; the first because we are to determine the total sulphur, the second because it may carry down phosphoric acid with it. In either event fuse this residue and leach out the fusion with water (no acid, or barium sulphate would re-form) filter and add the filtrate to the main solution. If a fine white precipitate should be formed at this point while the solution is still acid, it will be barium sulphate due to the presence of more than enough barium in the ore to combine with the sulphate and must be filtered out and added to any barium sulphate found as usual.*

Pour the main solution into an excess of ammonia diluted with water in a large beaker, heat, filter and wash first by decantation and then on the filter with hot water till free from chlorides. Evaporate the filtrate down to about 200 c.c., acidify and precipitate the sulphur as barium sulphate, using the conditions given under coal analysis.

Treatment of Precipitate containing iron, aluminum and phosphoric acid, also in some cases manganese, titanium, chromium, arsenic, etc. Transfer as much as possible of the precipitate to a No. 3 or 4 beaker and place it under the funnel, pour through the paper hot dilute nitric acid till all the adhering precipitate is dissolved, allowing the solution to run into the beaker containing the bulk of the precipitate, add more nitric acid and heat till the precipitate has dissolved, neutralize with ammonia till the solution is deep red in color but clear, then add nitric acid again till the red color is just changed to orange, add ten grams of ammonium

* The precipitation may not be complete on account of the acidity of the solution.

nitrate and warm the solution to about 60° C., add 100 c.c. of molybdate solution,* and allow to stand for half an hour at a temperature of about 45° C. If the operation is to be hastened the precipitation can be done in a flask and shaken for five minutes, wrapped in a towel to prevent cooling, then allowed to stand for another five minutes and the precipitation will be complete, unless the amount of phosphorus present is only 0.01 per cent. or less. Filter and wash with water to which 1 per cent. nitric acid and 10 per cent. ammonium nitrate have been added until the washings give no brown coloration with hydrogen sulphide, showing the complete removal of molybdenum.

We have now, the yellow crystalline ammonium phospho molybdate, $(NH_4)_3PO_4.12MoO_3$, washed free from molybdenum and iron; dissolve this in 100 c.c. of dilute ammonia (1 part 0.9 sp. gr. to 10 of water) nearly neutralize with hydrochloric acid, cool thoroughly and add slowly (not faster than 10 c.c. a minute), with stirring, an excess of "magnesia mixture." † The amount is judged by the quantity of the "yellow precipitate" and should be 1 c.c. for every 10 mgs. of phosphorus pentoxide present. Stir briskly until the precipitate appears then add about 8 c.c. of strong ammonia. The precipitate is allowed to stand in the cold for at least four hours, filtered, washed with ammonia (1 : 10, containing about 2.5 per cent. NH_3), ignited as already described, heated with the blast lamp and weighed. The percentages of sulphur and phosphorus are reported in an iron ore, not the percentages of SO_3 and P_2O_5.

Notes, Reasons and Properties of Precipitates.

Some authorities recommend the fusion of the entire five grams to begin with. There are two important objections: First, the

* The molybdate reagent is made as follows: 100 grams of molybdic anhydride (MoO_3) are mixed with 400 c.c. of distilled water and 80 c.c. of strong ammonia added, the solution of ammonium molybdate is filtered, to remove silica and dust, and poured a little at a time, into a mixture of 300 c.c. of nitric acid 1.42 sp. gr. and 700 c.c. of water; then one c.c. of a ten per cent. solution of sodium phosphate is added to saturate the solution with the "yellow precipitate" and the reagent is allowed to stand over night. The nitric acid must not be poured into the molybdate, as it will give a separation of molybdic acid near the neutral point which is difficult to redissolve. For the same reason the ammonium molybdate should not be added to the nitric acid all at once on account of the heat produced in the neutralization.

† The "magnesia mixture" is made by dissolving 55 grams of magnesium chloride and 70 grams of ammonium chloride in a liter of dilute ammonia, 1 to 10.

cost of the platinum crucible large enough to do it in; second, the introduction of 30–35 grams of alkali chloride into the solution at the start which interferes with clean separations and makes longer washing necessary.

The *dehydration of silica* is an operation of the greatest importance in analytical chemistry and is usually the first step after solution is obtained. If the silica is not removed completely and at once it comes down gradually and contaminates the subsequent precipitates. Then we do not know whether the silica which may contaminate the $Mg_2P_2O_7$ precipitate is from the ore or from the action of the solutions on the beakers. Ores contain silica as quartz and as silicates of lime, magnesia, iron, etc. Some of these are soluble and others are not, depending on the particular minerals, so that the original solution of the ore may contain silica in solution and the residue insoluble silicates besides silica; when fused with alkali carbonates these give soluble alkali silicates which on acidifying give silicic acids. The evaporation and baking drives the water off these silicic acids, H_2SiO_3, H_4SiO_4, etc., giving when dried at about 100° $SiO_2 \cdot \frac{1}{2}H_2O$ which is nearly insoluble. This we filter out, but it must be heated by a blast lamp before weighing to drive off the last half molecule of water. It is not to be inferred that one evaporation is sufficient to effect an absolutely complete separation of silica, although it usually suffices for iron ores. Care must be taken not to allow the temperature to go above 120° as there is danger of the re-formation of silicates above 140°, particularly if magnesium is present.

Conditions for Precipitating the Ammonium Phosphomolybdate. — The solution should be slightly acid with nitric acid and contain 20 grams of ammonium nitrate, no tartrates or other organic compounds, and preferably no chlorides or sulphates. The acidity is of great importance; if too acid, the precipitation is slow and often incomplete; if too near the neutral point, the separation from iron is incomplete, and reddish crusts containing iron may form. These are insoluble when the phosphomolybdate is dissolved in ammonia, but may retain phosphorus and must be dissolved in nitric acid and the phosphorus reprecipitated as ammonium phosphomolybdate. In regard to temperature; if too hot (85° or over), or if allowed to stand for a long time, the precipitate is liable to be contaminated

by the separation of molybdic acid; if too cold, say 20°, the precipitation is slow. The best temperature is about 45°, for the reasons given, and also on account of arsenic. When this is present and the temperature is high an arseniomolybdate similar in composition to the phosphomolybdate separates and gives too high results, as it forms with magnesia mixture an insoluble magnesium ammonium arsenate similar to the magnesium ammonium phosphate. Reducing agents and silica should be absent; the latter comes down as hydrated silica, but not as a silicomolybdate.

Solubility of Ammonium Phosphomolybdate. — Readily soluble in ammonia and other alkalies, in alkali phosphates; soluble in hydrochloric acid, strong sulphuric and nitric acids; very slightly soluble in water. Best washed with 1 per cent. nitric acid and 10 per cent. ammonium nitrate, or 1 per cent. sulphuric acid and 10 per cent. ammonium sulphate.

There is no longer any doubt as to the composition of this precipitate when formed under the conditions given, though it may carry down with it somewhat uncertain but relatively small quantities of nitric acid and water of crystallization. When carefully precipitated it may be dried for half an hour at 120° C. and weighed; it then contains 1.63 per cent. of phosphorus.

In dissolving the precipitate very dilute ammonia is used for two reasons: (1) that ammonium molybdate is not very soluble in ammonia, (2) to avoid a great excess of ammonium chloride in the subsequent precipitation.

Magnesium Ammonium Phosphate can be obtained under three different conditions, according to Neubauer.

1. The precipitate is formed in a neutral or ammoniacal solution containing no excess of magnesium salt. Result, the precipitate contains less than the normal amount of magnesium and phosphorus pentoxide is volatilized on ignition. Results low.

2. The precipitate is formed in the presence of an excess of magnesium salt but during its formation ammonia is not present in large excess. Results correct.

3. The precipitate is formed in the presence of an excess of both magnesium and ammonia. Results high.

The other precautions in regard to treating this compound have been given under magnesium sulphate.

There is no advantage in using separate portions for sulphur or phosphorus as they may not be entirely soluble in acids so that when the silica is removed no time is saved. The insoluble phosphorus is supposed to be combined with aluminum and can be rendered soluble by a strong ignition previous to treating with acids.

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CHAPTER VII.

Pig Iron and Steel Analysis.

Determination of Phosphorus.

The phosphorus in iron or steel, unlike that in ores, exists as a phosphide, so the first step in the analysis is an oxidizing treatment, solution in nitric acid, with this exception the method given for iron ore can be applied to steel and to pig iron after filtering off the graphite, etc., but the method is too long for the demands of a metallurgical plant and the "permanganate method" is very generally used. This method has many slight variations but the essential features are always the same. The following description most nearly approaches the methods of W. A. Noyes and Blair.

Reagents: Nitric acid, 1.18 sp. gr.

Permanganate solution, 12.5 grams per liter.

Ferrous sulphate in fine crystals free from phosphorus (Baker and Adamson).

Ammonia conc. 0.9 sp. gr.; dilute 0.96 sp. gr.

Molybdate solution as described under iron ore.

Washing solution: Acid ammonium sulphate, made by adding 27.5 c.c. of dilute ammonia (0.96 sp. gr.) and 24 c.c. of concentrated sulphuric acid to water and diluting to one liter.

The standard permanganate already described.

Method: Weigh out 2 grams of steel or 1–2 grams of pig iron; place in a 500 c.c. flask; add 50 c.c. nitric acid (1.18 sp. gr.) and warm gently till solution is complete, then boil for a minute (with pig irons there will remain a black residue of graphite), add 10 c.c. of the strong permanganate solution and boil till the pink color disappears. The permanganate is added to complete the oxidation of the phosphorus which must be present entirely as an orthophosphate in order to be precipitated as phosphomolybdate. On boiling, the manganese separates from the permanganate as hydrated dioxide. This is cleared up by a reducing agent free from phosphorus, *i. e.*, ferrous sulphate, added in small portions till the solution clears (with pig iron the graphite remains). At this point,

with pig irons, it is best to filter out the graphite, etc., so as to have a clear solution for the precipitation of the phosphomolybdate and also to save time in the filtering and washing. Cool to about 50° C., and neutralize with ammonia until the solution is deep red in color but remains clear, then add dilute nitric acid until the red color changes to orange. Cool or warm the solution until it is as many degrees above or below 60° as the molybdate solution is below or above 27° (so that when mixed the temperature will be approximately 45° C.). Add 60 c.c. of the molybdate reagent, insert the stopper, wrap in a towel to prevent cooling and shake vigorously for five minutes, allow to settle for five minutes and filter through a 9 cm. paper. Wash from the top down with the acid ammonium sulphate solution until 5 c.c. give no brown coloration with hydrogen sulphide water (showing the complete absence of molybdenum). Pour over the precipitate 12 c.c. of ammonia (0.96 sp. gr.) diluted to 25 c.c. and allow the solution to run into the precipitation flask. Wash with 100 c.c. water, then add 80 c.c. more water and 10 c.c. of conc. sulphuric acid. Pass this solution through a Jones reductor, with the precautions already described under ferric alum, follow it with 200 c.c. of water and titrate the solution at once in the reductor flask without dilution or delay.

Notes. — This method is entirely satisfactory for steels and, with the modifications given, works well for pig irons; it is not certain whether it is accurate for spiegel or for some special steels containing chromium, tungsten, molybdenum, etc., and should be checked up by the gravimetric method when used on such samples.

With pig iron the amount of ammonia to be used in neutralizing varies and in all cases some judgment must be used and the correct degree of acidity obtained. When only 0.01 per cent. of phosphorus or less is present, the neutralization must be closer and the time allowed for precipitation longer; with pig irons abnormally high in phosphorus (this is shown by the quantity of the yellow precipitate) more molybdate should be added. A difficulty often arises when the ammoniacal solution of the yellow precipitate is acidified — the precipitate separates out again. This can be remedied by more sulphuric acid, or better by redissolving in ammonia and making up to even bulk and taking an aliquot part

for acidification and titration. This will avoid the reprecipitation and also using perhaps several hundred cubic centimeters of permanganate.

The solution as it comes from the reductor should be olive green, the depth of color depending on the quantity of molybdenum. On adding permanganate different colors are formed as the oxidation progresses until finally the solution becomes colorless. It is a pink after this point, which marks the complete reoxidation to MoO_3 and is taken as the end point.

There has been much discussion as to the degree of reduction of the molybdenum after passing through the reductor. Under the conditions which follow, the reduction corresponds to an oxide $Mo_{24}O_{37}$.

There is no evidence of the existence of such an oxide, nor is there a definite stopping point corresponding to this degree of reduction, but under certain conditions the reduction proceeds to this point, viz.: Length of column of 20–30 mesh zinc, 37 cm.; time of passage, about six minutes; temperature, 70°–75° C.; volume, 200 c.c.; acidity, 10 c.c. of concentrated sulphuric acid. The factor for converting the iron standard of the permanganate to the phosphorus standard, based on reduction to $Mo_{24}O_{37}$ is 0.01584; while the factors as determined experimentally* are 0.01579 for unamalgamated and 0.01586 for amalgamated zinc.

The factor 0.01538 corresponds to a complete reduction to Mo_2O_3 and should be used when the molybdenum is reduced as follows: Dissolve the yellow precipitate in ammonia and allow it to run back into the precipitation flask to dissolve what adheres to the sides; the volume is now about 75 c.c.; add 5 grams of pulverized zinc, 100 mesh, and 15 c.c. of conc. sulphuric acid. Close the flask with a rubber stopper provided with a bent tube dipping into a saturated solution of sodium bicarbonate (compare solution of iron wire). Allow to stand for half an hour, then if all action is over and the temperature is about 40° C. it is ready for titration by permanganate. A blank must be run on another portion of 5 grams of the same zinc with the same amounts of ammonia and sulphuric acid and the amounts of permanganate consumed by the iron present deducted from each determination made.

* Miller and Frank, *Jour. Amer. Chem. Soc.*, 25, 925, 1903.

Carbon Determinations.

Steel contains carbon combined with iron, forming different carbides of which cementite, Fe_3C, is one of the most important. Cast iron, in addition to these, contains graphitic carbon. When cast iron or steel is treated with strong acid the combined carbon is liberated as a hydrocarbon, which is volatile, and so a portion is lost.

When the *total carbon* is to be determined proceed as follows: Weigh out 1 gram of pig iron; place in a No. 2 beaker; add 100 c.c. of a solution of copper potassium chloride (containing 300 grams per liter) and 7.5 c.c. of concentrated hydrochloric acid. For steel, take 3 grams, 200 c.c. of the double chloride solution and 15 c.c. of concentrated hydrochloric acid. Stir the solution at the ordinary temperature until the iron is dissolved, then heat to about 60° C. and stir till the precipitated copper has gone into solution; allow to settle and filter through ignited asbestos in a small funnel or perforated platinum boat; wash with hot water, dry, and burn the carbon to carbon dioxide in a combustion furnace with oxygen, or in a flask by chromic and sulphuric acids; absorb the carbon dioxide in either potassium or barium hydroxide solution or by soda lime, and from the increased weight calculate the total carbon.

For details see Blair, and Cairns' Quantitative Analysis.

The reactions which take place are

$$Fe + CuCl_2 = FeCl_2 + Cu.$$
$$Fe_3C + 3CuCl_2 = 3FeCl_2 + 3Cu + C.$$
$$Cu + CuCl_2 = 2CuCl.$$

The potassium chloride, giving double salts, only hastens the solution.

When the hydrochloric acid exceeds 20 per cent. there is loss of combined carbon.

Graphite is most accurately determined by dissolving 3–5 grams of pig iron in nitric acid 1.2 sp. gr., using 15 c.c. for each gram taken, filtering through ignited asbestos and then washing with hot water, hot potassium hydroxide solution (1.1 sp. gr.), hot water, dilute hydrochloric acid, alcohol, ether and finally hot water; then burning to carbon dioxide.

These solutions are used to remove iron salts, silica, hydrocarbons, and the final washing with water is to remove alcohol.

This method is long and for rapid work and approximate results the following may be used. *Crobaugh's method modified.** Weigh 2–3 grams of drillings and transfer them to a 125 c.c. platinum dish, add 100 c.c. of nitric acid 1.135 sp. gr. and warm to hasten solution then add about 8 c.c. of 40 per cent. hydrofluoric acid (B. & A.) and heat for ten minutes. Filter at once on balanced filters, wash with water four times, then twice with hydrochloric acid 1 : 1 or till all iron is removed; then with ammonia 0.96 sp. gr. until the washings are colorless, to remove hydrocarbons, then again with hydrochloric acid and finally with water. Separate the two papers and dry them at 100°–105° C., place one on each pan of the balance and weigh the graphite. Then as a precaution burn them and the graphite in a weighed platinum crucible and deduct any residue found from the weight of graphite. Also examine this residue to see whether any iron compound has resisted solution.

Balanced papers are obtained by taking two from the same package, which have been adjacent and so presumably contain the same amount of moisture, and placing on the two pans of the balance, to determine which is the heavier, then cutting narrow strips off the edges of the heavier till they balance. They are then folded separately and placed one inside the other and the original solution, as well as all washing solutions passed through both. The assumption is made that as they weighed the same in the beginning and have been treated in the same way throughout, when dried at the same temperature they ought still to weigh the same.

Combined carbon in steel is most rapidly determined by a color comparison as follows:

Weigh out 0.2 gram of the sample and 0.2 gram of a standard steel in which the carbon has been accurately determined by the combustion method, and which is made by the same process and is in the same physical condition, into test-tubes 15 cm. long; add slowly the proper amount of nitric acid 1.2 sp. gr.; for steels containing less than 0.3 per cent. carbon use 3 c.c.; 0.3–0.5 per cent. 4 c.c.; 0.5–0.8 per cent. 5 c.c., and so on; place on the top of each test-tube a small glass funnel or marble, put the tubes in a water-

* *Jour. Amer. Chem. Soc.*, 16, 104.

bath and heat to boiling, then boil till all carbonaceous material has dissolved, shaking occasionally. This requires 20 to 45 minutes. Pour into graduated tubes and dilute one or the other till the colors match. For example, if the standard steel contained 0.4 per cent. carbon and when diluted to 8 c.c. matched the other steel when diluted to 13 c.c., — the sample contains 0.65 per cent. carbon.

The entire method depends on having two steels which are almost exactly identical and then treating them exactly alike throughout. Reverse the position of the two tubes when they appear to match to see whether they still agree in color and so offset any peculiarities in eyesight.

Sulphur Determination.

Sulphur may exist in four different forms in pig iron:

1. That evolved as hydrogen sulphide on treatment with hydrochloric acid.

2. That which is evolved as an organic sulphide, $(CH_3)_2S$, etc.; which is neither absorbed by alkaline solutions nor oxidized by bromine to sulphate. It can be decomposed by passing through a red-hot tube mixed with carbon dioxide and then yields hydrogen sulphide.

3. That which is not attacked by hydrochloric acid but is oxidized by nitric acid or aqua regia; perhaps arsenic and titanium sulphides.

4. That which is unacted on by aqua regia and requires a fusion to obtain it in solution.

The methods for determining sulphur are usually classed as evolution or oxidation.

The evolution methods only get the sulphur in (1) but if all the sulphur is present in this condition they are accurate. The amount of sulphur in (2) is exceedingly small and is probably lost by any method in use.

The oxidation methods get (1) and (3) and if the residue is fused (1), (3) and (4).

It has been shown by repeated comparisons that the evolution methods are unreliable in general and can only be used on such material as is known to give up its sulphur by treatment with hydrochloric acid, *i. e.*, steel and pig iron from certain ores.

Oxidation Methods.

*Method of Noyes and Helmer.** — Put 200 c.c. of water and 8 c.c. of bromine (free from sulphur) in a flask and add 5 grams of iron or steel drillings in portions, cooling after each addition. Solution takes place readily, giving ferric bromide and sulphate. When it is complete boil to expel the slight excess of bromine, filter, and wash the residue, set aside the filtrate. To the residue add about 2 grams of sodium carbonate and burn the filter in a platinum crucible, using an alcohol lamp and completing the oxidation by the addition of a few crystals of potassium nitrate and re-ignition. Dissolve the residue in water, filter, acidify the filtrate with hydrochloric acid, add 5 c.c. of barium chloride solution, heat, etc., and weigh the barium sulphate; add three fifths of the weight of barium sulphate found here to that obtained from the filtrate. Place 130 c.c. of 10 per cent. ammonia (.96 sp. gr.) in a 500-c.c. flask and pour in the filtrate, dilute to the mark and mix thoroughly by pouring into a dry beaker and back; filter through a dry filter. Take 300 c.c. (three fifths) of the strongly alkaline filtrate and evaporate it in a wide beaker to about 100 c.c., taking care that it shall not absorb sulphur from the gas. Then add five or six drops of dilute hydrochloric acid and precipitate the sulphur as barium sulphate in the usual manner. To the barium sulphate so obtained add three fifths of that from the residue and calculate the results on three grams of steel.

Notes. — This method is both accurate and rapid. It obtains all but the organic sulphide which may be present. It overcomes the difficulty of washing out the sulphate from the bulky ferric hydroxide from five grams of iron, by taking an aliquot part, and the many troubles which arise when the attempt is made to precipitate barium sulphate in the presence of iron.

In some cases more than 8 c.c. of bromine are required to effect complete solution. The iron should be added slowly and in portions, so as not to heat the solution by a violent reaction and so cause a separation of a basic ferric salt, which is redissolved with difficulty.

The only possible objections to this method are, the error due to the volume of the precipitate when an aliquot part of the filtrate

* *Jour. Amer. Chem. Soc.*, 23, 675, 1901.

is removed, which is practically nothing with material so low in sulphur, and the possibility of contamination of the barium sulphate from the residue by hydrated silica.

Bamber's Method is equally accurate, but less convenient. Dissolve at least 5 grams of the sample in strong nitric acid; add 2–5 grams of potassium nitrate; evaporate to dryness in a platinum dish and ignite. Boil with water and sodium carbonate, filter and wash with water containing sodium carbonate. Acidulate the filtrate with hydrochloric acid, evaporate to dryness to dehydrate the silica, redissolve in water and a few drops of hydrochloric acid, filter and determine as barium sulphate. For further details see Blair or *Jour. Iron and Steel Inst.*, 1894, p. 319.

Sulphur is also determined * by precipitation as barium sulphate in the presence of iron, but the method is open to serious objections. On account of the solubility of barium sulphate in hot acid solutions containing ferric chloride the precipitation must be made in a solution only warm and then must be allowed to cool before filtration. Under these conditions the precipitate is not only difficult to filter, but is usually contaminated by iron. The cause of the contamination as given by Kuster and Thiel † is the formation of the insoluble barium salt of a complex ferrisulphuric acid, $Ba(Fe_2S_2O_8)_2$, which loses SO_3 on ignition, so the contaminated barium sulphate may give too low, not too high results, and the purification of the precipitate only increases the inaccuracy. This trouble can be avoided by precipitation in the cold or by pouring the ferric solution into the barium chloride, but it is preferable to remove the iron as given in the methods described.

Evolution Method. Camp's ‡ Description of the Elliott Method.

Solutions Required.

Iodine. — Weigh into a flask about 18 grams of potassium iodide and 8 grams of iodine; add water and shake till solution is complete, then dilute to about 1.75 liters. This is standardized by steels containing known amounts of sulphur.

* Colby's method as given in Cairns, p. 170.

† *Zeits. anorg. Chem.*, **22**, 424.

‡ Phillips' "Methods of Iron Analysis," p. 41.

Cadmium Chloride. — Dissolve 12 grams of cadmium chloride in about 125 c.c. of water, add 65 c.c. of strong ammonia and filter into a liter bottle; 250 c.c. of water are added and the solution made up to a liter with strong ammonia.

Starch Solution. — Add to half a liter of boiling water in a liter flask, 3–4 grams of pure starch, previously stirred to a thin paste with cold water; this is boiled for ten minutes, and when cold 3–4 grams of pure zinc chloride are added and the solution diluted to a liter with cold water. The clear solution is siphoned off for use and keeps well.

Method. — Five grams of pig iron or steel are weighed off into a dry half-liter flask, provided with a two-hole rubber stopper, with funnel tube and delivery tube with a rubber-tube connection, which is connected with a glass tube which reaches to the bottom of a test-tube 2.5 cm. wide and 25 cm. deep. In this is placed 10 c.c. of the ammoniacal cadmium solution, diluted with water so that it fills two thirds of the test-tube. Eighty c.c. of hydrochloric acid 1 : 2 (1.07 sp. gr.) are now poured into the flask through the funnel tube and a gentle heat applied till all the iron has dissolved, then heated to boiling until nothing but steam escapes. The apparatus is then disconnected and the delivery tube placed in a No. 4 beaker, and the contents of the test-tube poured in, then the test-tube is rinsed out with 25 c.c. of dilute hydrochloric acid and with water and the rinsings added to the beaker; the volume of the solution should be about 400 c.c. When the cadmium sulphide has dissolved, 0.5 c.c. of starch solution is added and the standard iodine run in till a permanent blue color is obtained. The iodine can be adjusted to read one hundredth of a per cent. of sulphur for each cubic centimeter when 5 grams are taken for analysis.

The chemistry of the process is as follows: The sulphur is liberated as hydrogen sulphide; this is absorbed by the ammoniacal cadmium solution, giving yellow cadmium sulphide, which is easily dissolved in dilute hydrochloric acid, giving hydrogen sulphide again which remains dissolved in the large volume of water present, 400 c.c. The iodine solution reacts $H_2S + I_2 = 2HI + S$, in a dilute solution. Then the least excess of iodine gives an intense blue with starch which is the end point.

Silicon Determination.

Drown's method or some modification is always used. Treat one gram of borings with 20 c.c. of nitric acid 1.2 sp. gr. in a platinum or porcelain dish or casserole. When all action has ceased add 20 c.c. of sulphuric acid 1 : 1 and evaporate to copious fumes of sulphuric anhydride, allow to cool and dilute carefully with 150 c.c. of water, heat to dissolve ferric sulphate, filter hot and wash first with hydrochloric acid 1 : 1 and then with water till free from iron. Burn off the carbon in a weighed platinum crucible and weigh the SiO_2; check by driving it off with hydrofluoric acid.

Notes. — Nitric acid should be used, not hydrochloric, as there may be a titanium carbide present which is not attacked by hydrochloric acid alone. A modification is to add both acids at once, *i. e.*, nitro-sulphuric acid. This is made by adding 60 c.c. of conc. sulphuric acid to 600 c.c. nitric acid 1.2 sp. gr. Thirty c.c. are used for each gram of drillings.

The sulphuric acid takes the water from the silica and so renders it insoluble. This method is more rapid than dehydration by means of heat alone but is limited in its application to those cases where insoluble sulphates are not present. Like the method described under iron ore, traces of silica escape when only one evaporation is made, but the quantity present is so small that a second dehydration is rarely necessary.

Determination of Manganese.

Manganese in steel is usually determined colorimetrically after oxidation to permanganic acid by lead peroxide in a nitric acid solution, but the method proposed by Walters * seems preferable. Weigh 0.2 gram of the steel to be tested and the same quantity of a standard steel of known manganese content into two large test-tubes. Add 10 c.c. nitric acid 1.2 sp. gr. to each and heat them in a water-bath till the nitrous fumes are driven off. Next add 15 c.c. of a solution of silver nitrate containing 1.33 grams to the liter, and then immediately about a gram of moist ammonium persulphate, $(NH_4)_2S_2O_8$, to each; continue heating till the oxidation is complete, then half a minute longer. Remove the tubes, while

* Walters, *Chemical News*, Nov. 15, 1901.

the oxygen continues to come off, and place them in cold water. When cool compare the colors as described under combined carbon.

Notes. — When the manganese is over 0.75 per cent. use only 0.1 gram of steel. The ammonium persulphate loses its efficiency unless it is kept moist. The method can be applied to pig iron by filtering off the carbon, etc., or can be changed to a volumetric method by titrating the permanganate by a standard arsenite solution as described by Stehman in the *Journal of the American Chemical Society* for December, 1902.

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CHAPTER VIII.

Determination of Manganese in Spiegel and in Manganese Ores.

VOLHARD'S METHOD.

This is based on the following reaction which takes place in a hot dilute neutral solution containing zinc sulphate or nitrate, in which the manganese is present as sulphate or as nitrate:

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

The neutrality is maintained by the excess of zinc oxide present. Many modifications of the original method have been proposed, neutralizing with barium carbonate, sodium bicarbonate, etc., but the only change which is an improvement is Stone's use of nitric acid in the case of spiegels.

The tenth normal permanganate solution may be used again here or if one is to be made up especially, 2 grams per liter is a convenient strength. The manganese standard can be calculated from the iron standard, but it is preferable to standardize against a spiegel of known manganese content.

Manganese Ore. — Treat one gram of the manganese ore, ground extremely fine, in a casserole with 10 c.c. of concentrated hydrochloric acid and if necessary a little nitric acid to ensure the oxidation of the iron present. When pyrolusite, etc., are to be analyzed of course the nitric acid is unnecessary; heat till complete decomposition is effected, then add 25 c.c. of water and 5 c.c. of concentrated sulphuric acid and evaporate to fumes of sulphuric anhydride; cool, dilute to about 150 c.c. and heat to dissolve the sulphates completely. Examine the insoluble residue to see whether it is completely decomposed; if not, as would be the case with franklinite, filter; fuse the residue with mixed carbonates, dissolve in hydrochloric acid, evaporate to fumes with sulphuric acid and add the solution, after diluting, to the main portion.

Nearly neutralize the sulphate solution with a saturated solution of crystallized sodium carbonate, transfer to a liter flask and add a

cream of zinc oxide (free from manganese) until the precipitate of ferric hydroxide, etc., settles rapidly; shake after each addition of zinc oxide, so as not to use an unnecessary excess. Allow the solution to cool and dilute to the mark. Mix thoroughly by pouring into a large beaker and back into the flask; it makes no difference whether any is lost after mixing, as only portions are taken for titration. Either filter through a dry paper and take out portions of 100 or 200 c.c. each, depending on the richness of the ore, or withdraw such portions by a pipette from the cloudy liquid above the brownish precipitate in the flask.

Place the portions in small casseroles and if 100 c.c. is taken dilute it to about 200 c.c. with water. Heat to boiling, and while hot run in permanganate rapidly, 1 c.c. at a time, stirring vigorously with a bent glass rod till a faint pink is seen against the side of the casserole after the precipitated manganese dioxide has settled; then stir hard again to make sure that the color is permanent, for it sometimes stirs out and then more permanganate is required. The first portion is run rapidly to get an idea of the amount required, the others quickly up to within 1 c.c. of the amount used on the first titration; then carefully, a drop at a time, till the faint permanent pink color is obtained. The reason for this is that when the permanganate is run in slowly the dioxide adheres to the sides of the casserole, so that there is no longer a good back-ground for the end point, and also because the solution becomes cold, which renders the reaction less prompt. Several portions can be run from the original gram till satisfactory duplicates are obtained.

With spiegel the method can be made even shorter. Dissolve one gram in about 25 c.c. of nitric acid, 1.2 sp. gr.; boil out fumes, etc., neutralize with sodium carbonate solution, and proceed as described.

Notes. — The original Volhard method required sulphates, but it has been shown that nitrates are permissible but chlorides objectionable. As manganese dioxide is insoluble in nitric acid we can not use this acid for the solution of all manganese minerals and so Volhard's method is given for ores.

Neutralizing by sodium carbonate is carried on till a reddish color is produced but no precipitate. The zinc oxide is ground up

in a porcelain mortar with water and the creamy liquid poured off for use. Lumps of zinc oxide are of no use and by occupying space cause an inaccuracy when we withdraw say one fifth of the solution and consider that it contains the manganese from one fifth of the amount taken. Notwithstanding the error introduced by the volume of the precipitate and of the zinc oxide it is better not to allow for them as there is another cause of error which this partly compensates. The precipitate formed by the permanganate is not always exactly hydrated MnO_2; it may be very slightly deficient in oxygen. So the best method is to standardize on a similar spiegel or ore in which the manganese has been determined gravimetrically rather than to calculate from the iron standard. Barium carbonate can be used to neutralize but the end point is not as sharp as with zinc oxide. There has been much discussion as to the excess of zinc oxide and the manner of adding it; probably it is best to add but a slight excess in order to precipitate the iron and then after dilution to add more. It is however important to do this the same way each time and exactly as in standardizing.

Chlorate Separation (Hampe).

This depends on the fact that the addition of crystals of potassium or sodium chlorate to a solution of manganese in strong nitric acid precipitates the manganese as dioxide on boiling. If iron is present a small amount precipitates with the MnO_2. Chlorides must be absent or the precipitation is incomplete.

The nitric acid solution is boiled down to expel other acids, etc.; 75 c.c. of concentrated nitric acid are added and the solution heated, then 3–4 grams of chlorate, then heated to boiling for ten minutes, allowed to cool somewhat and another portion of chlorate is added, followed by another boiling; after cooling, the dioxide is filtered on asbestos and washed with strong nitric acid, then with water. The oxidizing power of the precipitate can be determined or it can be dissolved and the manganese determined gravimetrically after the removal of the iron. The method is used for spiegel, etc., and is useful for separating small amounts of manganese from large quantities of iron in pig iron, etc. See Ford's and Williams' methods in Blair's "Chemical Analysis of Iron."

Gravimetric Method for Spiegel.

Dissolve one gram of the finely ground sample, for spiegel is brittle and can be pulverized in a harveyized steel mortar, in about 15 c.c. of nitric acid, 1.2 sp. gr., in a small beaker, evaporate to dryness and bake to decompose the hydrocarbons and dehydrate the silica; add 20 c.c. of hydrochloric acid 1 : 1 and heat till the iron is all dissolved; evaporate nearly to dryness to expel nitric acid; take up with water and hydrochloric acid, if necessary to give a clear solution, and filter out the residue of silica, etc. We now have the iron as ferric chloride, the manganese as manganous chloride in a bulk of about 100 c.c. slightly acid with hydrochloric acid and no nitrates present. To this solution add a solution of crystallized sodium carbonate till a very slight permanent precipitate is formed; dissolve this in a few drops of dilute hydrochloric acid. Transfer the clear deep red solution to a large beaker and dilute with cold water to about 700 c.c.; the solution should remain clear. Add one gram of sodium acetate (3 c.c. of a saturated solution), heat to boiling as quickly as possible and boil for three minutes; slow heating or long boiling gives a slimy precipitate which is hard to filter. Filter through a fluted paper and wash with boiling water. The solution must be filtered hot, as the precipitate is likely to redissolve in the acetic acid present if allowed to cool. Redissolve the precipitate in hot dilute hydrochloric acid and repeat the "basic acetate" precipitation. Combine the filtrates and evaporate them to about 350 c.c.; if any iron separates, filter, dissolve this in hydrochloric acid and make a small basic acetate precipitation to recover any manganese present; combine the filtrates.

Notes on the "Basic Acetate" Separation.

This is one of the oldest and most important separations in analytical chemistry, and depends on the hydrolytic action of boiling water. It serves for the separation of the triad elements, iron, aluminum, chromium, etc., from the dyad elements manganese, zinc, cobalt, nickel, etc. It is evident therefore that all the iron must be in the ferric condition and the manganese in the manganous, for ferrous iron is not precipitated (dyad), while manganic manganese is. This condition is readily obtained by boiling the solu-

tion after oxidation which quickly decomposes the unstable higher chlorides of manganese. The separation may be complete from zinc but has to be repeated to ensure absence of manganese from the precipitate which is likely to retain nickel, cobalt or copper even after several reprecipitations.

Ferric iron is a weak base. We first neutralize nearly all of the free acid (HCl), then add sodium acetate which forms sodium chloride and free acetic acid; the iron is also largely converted to acetate, as is shown by the deep, blood-red color which is formed at this point. The solution is now ready for the hydrolysis. The rule for dilution is 100 c.c. for every 0.1 gram of iron present, *i. e.*, for 1 gram of spiegel 700–800 c.c. The reagent is in reality boiling water, which, now that we have the ferric iron combined with the weak acid (acetic), reacts, giving a basic acetate of iron and free but largely undissociated acetic acid.

The composition of the precipitate is not uniform as the replacement of $C_2H_3O_2$ groups by hydroxyl goes on as the boiling progresses. It may be $Fe_2(OH)_2(C_2H_3O_2)_4$, $Fe_2(OH)_3(C_2H_3O_2)_3$, etc. If the boiling is excessive two troubles may arise; the precipitate with many (OH) groups, approaching the hydroxide, is slimy and the acetic acid in solution may reach a concentration where the reverse reaction takes place and the precipitate dissolves. This is most likely to result if the solution is allowed to cool, for then the hydrolytic action is less strong and the reverse action has a chance to progress until equilibrium is again established, and we find iron in the filtrate. The filtrate should be tested for iron by a ferrocyanide, not by a thiocyanate, in this solution containing acetates.

Fresenius gives the dilution already mentioned and the acidity about one per cent. of absolute acetic acid. If too little acetic acid is present the hydrolytic action is too strong and manganese as well as zinc, nickel, cobalt, etc., come down with the iron, alumina, etc. Titanium, if present, is precipitated with the iron, also phosphorus, arsenic and vanadium in combination, as when ammonia is used.

By bearing in mind these principles it is easy to adapt the method to a manganese ore. Here the iron is low, the manganese higher. The chloride solution is neutralized in small volume, the red color will be faint, then diluted somewhat — probably 200 c.c.

will be sufficient — then less sodium acetate is added, about half a gram, with perhaps a little acetic acid.

With ferromanganese the procedure is similar, for the manganese is 3–4 times the iron. In the case of an iron ore, when manganese is to be determined, this separation is substituted for the ammonia precipitation, then the manganese is taken out of the filtrate by bromine and the filtrate used for lime and magnesia as will be described under limestone.

The method is of very general application, but must be adapted to the particular analysis. The precipitate is never ignited and weighed, on account of the alkaline salts, etc.: if the oxides and phosphates of iron, aluminum, etc., are to be weighed together as in an iron ore, the basic acetate precipitate is dissolved in hydrochloric acid and reprecipitated by ammonia. It is not advisable to determine sulphur in the filtrate from this method on account of the likelihood of there being sulphur in the reagents.

The description of the gravimetric determination of manganese is taken up in general from this point.

Removal of Nickel and Cobalt.

To the solution in a casserole add ten grams of sodium acetate and a few drops of acetic acid so as to give a solution but faintly acid with acetic; heat to boiling and pass in hydrogen sulphide while hot. This will precipitate the sulphides of nickel, cobalt, zinc and copper if present; and manganese ores often contain cobalt. When the solution is saturated with hydrogen sulphide, digest for a time hot, then filter, and wash with hydrogen sulphide water.

Cobalt and nickel are often present and must be removed before we throw down the manganese by bromine, for they also give black higher hydroxides. The conditions for their precipitation as sulphide must be carefully maintained.

Manganous sulphide is soluble in hydrochloric and acetic acids; zinc sulphide is soluble in hydrochloric not in acetic acid.

Nickel and cobalt sulphides, when once formed are insoluble in either hydrochloric or acetic acids, but are prevented from precipitating by either acid in the cold and by hydrochloric or much acetic acid when hot. However when hot and the acetic acid

rendered weak by the mass action of the sodium acetate, nickel and cobalt sulphides will precipitate. If they are contaminated by manganous sulphide this can easily be leached out by washing with hydrochloric acid 1.025 sp. gr. saturated with hydrogen sulphide.

The explanation of the strange action of these sulphides is that they exist in two modifications — a soluble and an insoluble — and that on standing or on heating the soluble, which forms first, is converted into the insoluble, which then requires aqua regia for its solution.*

Precipitation of Manganese by Bromine.

The next step is the precipitation of the manganese by bromine. This might seem unnecessary in the case of a spiegel where there are no salts of lime, magnesia, zinc, etc., which give insoluble phosphates, but there is such an accumulation of sodium salts, etc., that a reprecipitation of the manganous ammonium phosphate is necessary, so that it is a better plan to throw out the manganese as dioxide. Boil out the hydrogen sulphide from the filtrate, allow it to cool and add 2–3 c.c. of bromine (not bromine water); heat to expel the excess of bromine and filter; to the filtrate add a few drops of bromine and a little sodium carbonate to bring the solution nearly to the neutral point and heat again to insure complete precipitation of the manganese.

If the solution is too acid the first precipitation may not be complete; if insufficiently acid some manganese may be oxidized to permanganate. When this happens it can easily be reduced by heating with a few drops of alcohol or of sulphurous acid.

The hydrated manganese dioxide is washed with hot water, and then dissolved in a little hot hydrochloric acid 1 : 1 to which a few c.c. of sulphurous acid have been added to cause a ready solution of the dioxide giving manganous chloride (compare addition of stannous chloride in iron ores).

Sometimes in evaporating the filtrate from the basic acetate precipitate manganese dioxide separates out. If this is free from iron it can be filtered and added to the rest.

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* Herz, *Zeits. anorg. Chem.*, 28, 342, 1901.

Precipitation of Manganese as Phosphate.

There can be no doubt that of all the methods so far proposed for the determination of manganese this is the most accurate and satisfactory. To the hydrochloric acid solution add a decided excess, at least five times the calculated quantity of either microcosmic salt, $NaNH_4HPO_4$, dissolved in water or $(NH_4)_2HPO_4$ solution, which is readily prepared by neutralizing phosphoric acid with ammonia till it just turns phenol-phthalein pink; heat, then add ammonia until the precipitate forms but avoid an excess.

The first precipitate is somewhat flocculent and contains $Mn_3(PO_4)_2$; this is heated on the water-bath until it becomes crystalline and settles almost at once when stirred. The $MnNH_4PO_4.H_2O$ so formed is nearly white with a characteristic nacreous luster and is one of the easiest precipitates known to filter and wash. Allow the solution to cool and filter as usual, wash with water or better with a 1 per cent. solution of the precipitant, followed by dilute alcohol; dry, separate from the paper; burn the paper, moistened with nitric acid, add the precipitate, ignite strongly and weigh the manganous pyrophosphate, $Mn_2P_2O_7$. Or else filter on washed asbestos (amphibole not serpentine) in a Gooch crucible and weigh after drying to constant weight at 100°–105° C., as $MnNH_4PO_4$-H_2O.

Instead of asbestos, balanced or weighed filter papers may be used.

Notes.—Before applying this method of precipitation the manganese must be separated from all metals except the alkalies. In forming the precipitate there must be a sufficient concentration of NH_4 ions to change the Mn_3PO_4 formed at first to the $MnNH_4PO_4$; this is supplied by the great excess of $(NH_4)_2HPO_4$ or by the precipitant and NH_4Cl when microcosmic salt is used. Serpentine asbestos is soluble in the phosphate solutions and must not be used.

An excess of ammonia turns the precipitate brown. If this happens, dissolve in hydrochloric acid and reprecipitate.

It is best to separate this precipitate from the paper as it occasionally becomes reduced, giving a phosphide which damages the platinum.

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CHAPTER IX.

Determination of Zinc in Ores.

VOLUMETRIC METHOD BY POTASSIUM FERROCYANIDE.

Zinc is precipitated by potassium ferrocyanide in a solution, acid with hydrochloric, according to the reaction: $3ZnCl_2 + 2K_4Fe(CN)_6 = Zn_3K_2Fe_2(CN)_{12} + 6KCl$. The end point is shown by the formation of a brown color when a drop of the solution is placed in contact with a drop of a uranium solution, preferably the nitrate. The brown is caused by the formation of uranium ferrocyanide by the slight excess of potassium ferrocyanide. The method when properly carried out is rapid and yields very satisfactory results; anything which decomposes or oxidizes the ferrocyanide must be absent, *i. e.*, strong acids, chlorine, etc., and also all of the numerous metals which give insoluble or sparingly soluble ferrocyanides. Those most likely to be present in zinc ores are cadmium, copper, iron, manganese, nickel, cobalt, antimony and aluminum.

Solutions. — A standard solution of potassium ferrocyanide, made by dissolving 21.6 grams of the crystallized salt, $K_4Fe(CN)_6.3H_2O$, in cold water and diluting to one liter. One c.c. will be equivalent to about 5 milligrams of zinc; a 5 per cent. solution of uranium nitrate; a solution of ammonium chloride, 10 grams per liter.

Standardizing. — As the end point is not very sensitive, in the presence of hydrochloric acid, it is necessary to deduct from each reading the amount of the solution in excess necessary to give a certain color with the uranium nitrate. Further, as uranium ferrocyanide is soluble in hydrochloric acid, the excess required for a definite color is dependent on the acidity of the solution. Also the composition of the precipitate varies, depending upon whether the solution is alkaline (NH_4OH), neutral, acid with acetic, or acid with hydrochloric; and if the excess of hydrochloric acid is too great, 10 c.c. of concentrated or more, and the solution titrated nearly boiling, there is likely to result a decomposition with the

formation of blue precipitates or colors, which spoil the determination.

These considerations make it imperative to decide at once the best conditions for titration, and then to determine the allowance for the indicator under exactly these conditions.

The following are of the most general application: volume, 200 c.c.; acidity, 6 c.c. of concentrated hydrochloric acid; temperature, 70° C. (about); ammonium chloride present about 10 grams. The ammonium chloride is added as it affects the appearance of the precipitate somewhat and is usually present when the titration is made. It seems to sharpen the end point slightly. These conditions allow for the presence of lead, which is likely to be present from the ore or from the test lead used to remove copper, as 6 c.c. of hydrochloric acid in 200 c.c. completely prevent the precipitation of lead ferrocyanide. More hydrochloric acid makes the allowance for the indicator too large and too uncertain and so impairs the accuracy of the method.

When lead is absent, for ores like franklinite and certain sulphides containing no copper, it is preferable to decrease the acidity to 2 c.c. of concentrated hydrochloric acid and so decrease the allowance for the end point.

To determine the allowance add to a beaker a little less than 200 c.c. of water, 10 grams of ammonium chloride and 6 c.c. of concentrated hydrochloric acid and warm to about 70° C. Place a number of drops of the uranium nitrate solution on a white surface, tile or sized paper. Run in the ferrocyanide solution a drop at a time till, after stirring, the solution in the beaker gives a decided brown with the indicator. The amount used should be less than 0.5 c.c. This value must be determined with care as it is subtracted from the burette reading in every subsequent titration.

Zinc or zinc oxide can be used for standardizing. Really pure zinc is very difficult to obtain as it usually contains iron, arsenic and lead and often other impurities. Zinc oxide can be easily had free from these but should be freshly ignited and allowed to cool in a desiccator to insure the absence of carbonates.

Weigh out two or, better, three portions of ignited zinc oxide each 0.2–0.25 gram; dissolve these in No. 3 beakers in a little strong hydrochloric acid, dilute somewhat, add sodium carbonate

(or ammonia) till a slight permanent precipitate is formed, dissolve this in a drop or two of dilute hydrochloric acid, add the amount of acid decided on (6 c.c.), and 10 grams of ammonium chloride; dilute to about 180 c.c., heat to 70° C. and run in the ferrocyanide solution till the indicator is affected as before.

The precipitate is white and settles well when formed in a hot solution containing ammonium chloride, but without considerable experience there is no warning of the end. Here, it is easy to calculate approximately how much will be required and so avoid the tiresome addition of very small quantities; but in general it is better to divide the solution roughly in half, then titrate one half, adding a c.c. at a time, so as to get an idea of the quantity required. If the half took between 18 and 19 c.c. (no color at 18, strong brown at 19) we can add the other half and run up to 35 c.c. with safety and then finish with small additions till the end is reached.

Deduct the allowance for the end point and calculate the standards to the value of 1 c.c. in terms of zinc. They should not show a difference of more than one in the fifth decimal place.

There is a change in the character of the precipitate which seems to coincide with the completion of the reaction given, and so with the ferrocyanide used minus the allowance; this is not certain enough to be used as an end point, but after some experience it will indicate that the end point will be reached in a few tenths of a cubic centimeter.

There are two very different sources of zinc: (1) Zinc blende, sphalerite, with which may be classed the other soluble ores, Smithsonite, calamine, etc., of minor importance. The ore is likely to contain also lead in considerable quantity, always iron and often manganese, copper, cadmium and sometimes antimony. The ores from Wisconsin, Missouri, Virginia and the west all come under this class of soluble ores. (2) Franklinite, which occurs in large quantity in New Jersey. Associated with this mineral, there is also willemite and a zinc spinel. As this ore is not completely decomposed by acids and a large amount of manganese is present a different treatment is required. It is practically free from copper, cadmium, lead and antimony.

Method for Blende and other Soluble Ores.—Weigh out one gram of the finely ground ore and treat it in a casserole or Erlenmeyer

flask with 10–15 c.c. of hydrochloric acid, 1 : 1, then add 25 c.c. of strong nitric acid and evaporate to dryness, take up with dilute nitric acid, filter out silica, washing it several times with small portions of water, evaporate filtrate to about 10 c.c.; add more concentrated nitric acid and sodium or potassium chlorate, a few crystals at a time, boiling between each addition to throw out the manganese, and evaporate off all the liquid, but do not bake. Allow to cool, and when cold add 7 grams of ammonium chloride, 15 c.c. of ammonia and 25 c.c. of hot water; boil for a few minutes and break up any adhering particles so as to give the excess of ammonia and the ammonium chloride every opportunity of taking the zinc hydroxide into solution. Filter into a flask or beaker and wash the precipitate of ferric hydroxide, etc., well with the ammonium chloride solution, to which a few drops of ammonia have been added.

If there is a bulky precipitate of ferric hydroxide it will undoubtedly carry down zinc with it. Unless the precipitate is very small, dissolve it through the paper by hydrochloric and sulphurous acids into a clean casserole and evaporate down with nitric acid, then treat with chlorate, etc., as before; after washing the second precipitate, combine the two filtrates.

If the filtrate is blue copper is present. If cadmium is also present, neutralize the filtrate, heat and add 3 c c. of concentrated hydrochloric acid (no more)* and saturate with hydrogen sulphide to precipitate the sulphides of copper and cadmium which may be contaminated by some lead sulphide, filter and wash, and titrate the filtrate as already described. If copper is present but no cadmium, it can be most easily removed by acidifying with 10 c.c. of hydrochloric acid and shaking in a flask with about 30 grams of test lead (20 mesh) till the copper is precipitated, then decanting, washing and titrating as usual.

Aluminum foil is not good for this purpose as when much aluminum is in solution it is partially precipitated and makes the end uncertain. It is also likely to contain iron. The amount of alumina in ordinary ores does not interfere.

Antimony is not likely to be present. It would be removed by the treatment for cadmium.

* The volume is assumed to be about 150 c.c.

Notes. — Low * recommends the precipitation of the copper and cadmium as sulphides by hydrogen sulphide in a solution containing 6 c.c. of concentrated hydrochloric acid in a volume of 200 c.c. and the titration of the zinc in the presence of these sulphides as the acidity is sufficient to prevent the formation of much lead sulphide.

It has recently been stated by Waring † that cadmium is almost always present in the Missouri zinc ores in quantities from .25 to 2 per cent. and that it is extremely difficult to effect a satisfactory separation of zinc from cadmium by hydrogen sulphide without retreating the cadmium sulphide to free it from zinc. Also that the presence of cadmium is the cause of a slight discoloration in the ferrocyanide precipitate. In order to avoid the interference due to cadmium, Stone's method of precipitating the cadmium by aluminum foil in a sulphuric acid solution is used. This will, of course, precipitate copper as well, but involves the subsequent precipitation of the zinc as sulphide, to avoid the troubles caused by aluminum salts. The sulphide is dissolved in hydrochloric acid and titrated under the conditions given. Two cubic centimeters of acid will be enough here as there is no lead to be retained in solution and the allowance for the end point will be less.

Although arsenic does not interfere with the titration, it prevents the complete precipitation of iron by ammonia in excess and the excess can not be boiled out here, for then zinc would be precipitated as $Zn(OH)_2.H_2O$. So Low recommends treating the ore with bromine and hydrochloric acid until the arsenic is expelled as bromide.

Method for Franklinite. — Although nearly all the zinc in this ore can be dissolved by a treatment with concentrated hydrochloric acid, it is necessary to fuse the residue to get accurate results. There is also so much manganese and iron present that the chlorate and ammonia separations are not satisfactory.

Treat 2 grams of the sample as described for soluble ores, fuse the residue in platinum with about 10 parts of mixed carbonates, dissolve the melt in hydrochloric acid and dehydrate the silica if this is to be determined. Neutralize the filtrate with a saturated

* *Jour. Amer. Chem. Soc.*, 22, 198.

† *Jour. Amer. Chem. Soc.*, 26, 4.

solution of sodium carbonate till red, then add pure barium carbonate suspended in water till the iron is precipitated (like the zinc oxide in manganese ore). Make up to an even bulk in a flask, mix and withdraw portions for the determination of manganese and zinc.

A variety of methods can be used here; for rapid results, titrate one portion for manganese by Volhard's method (see Chapter VIII.), and in another after adding 1 c.c. of hydrochloric acid 1 : 7 titrate the total manganese and zinc by potassium ferrocyanide. (For details see Stone, *Jour. Amer. Chem. Soc.*, **17**, 473.) For more accurate work take 500 c.c., equivalent to 1 gram of ore, and precipitate the manganese by bromine in an acetic acid solution as already described, and in the filtrate, after boiling down to expel acetic and hydrobromic acids, titrate the zinc under the standard conditions. Here the 2 c.c. excess of hydrochloric acid is preferable to the 6 c.c.

Notes on the Barium Carbonate Separation. — Be sure that the barium carbonate used is free from sodium carbonate, which is used to precipitate it. This is done by boiling with a solution of barium chloride for several hours; the barium chloride gives barium carbonate with any sodium carbonate present, while the excess of barium chloride and sodium chloride do no harm.

Have only chlorides present; add the barium carbonate in the cold and withdraw portions or filter without allowing the precipitate to stand long. Under these conditions the following bases are precipitated, according to H. Rose: Al_2O_3, Mn_2O_3, Fe_2O_3, Cr_2O_3, TiO_2, CdO, CuO, As_2O_5, Sb_2O_5, P_2O_5 and others, either rare or not likely to be present.

On long standing, when hot, or when present as nitrate, some zinc is likely to be precipitated. It is well in any case to examine the precipitate for zinc and to reprecipitate if it is found.

In this method the barium carbonate precipitate can be used for the determination of iron volumetrically and the bromine precipitate for manganese either volumetrically or gravimetrically.

Gravimetric Method.

An outline of the plan to be pursued is: (1) Decomposition of the ore. (2) Dehydration of the silica. (3) Removal of the fifth

and sixth groups by hydrogen sulphide in weakly acid solution, bearing in mind the ready solubility of lead sulphide. (4) Reoxidation of the iron. (5) Precipitation of the iron, aluminum, etc., by either basic acetate or barium carbonate. (6) Removal of the manganese by bromine. These operations have been described.

Precipitation of the Zinc as Sulphide.

This is necessary because of the lime and magnesia which are usually present from the gangue of the ore, and which also give insoluble phosphates. Zinc sulphide must be precipitated under carefully regulated conditions so that it will filter rapidly, as it is liable to oxidize to sulphate on standing exposed to the air. The solution should be acid with acetic acid and warm, and contain about 15 grams of ammonium chloride, which favors its separation in a flocculent form which filters well. Like many other sulphides, it changes its form after precipitation, so it is best to saturate the solution with hydrogen sulphide and then allow it to stand in a warm place over night with a slow stream of the gas passing through, to prevent oxidation and insure complete precipitation.

Zinc sulphide may be precipitated from an alkaline solution, one barely acid with sulphuric acid, or from solutions of organic acids, citric, formic, etc., and, best by potassium sulphide, K_2S, from an alkaline cyanide solution (separation from nickel).

The sulphide should be washed with hydrogen sulphide water containing ammonium chloride or acetate to prevent its resuming a semi-colloidal condition and running through the filter. It is readily soluble in mineral acids and is likely to be contaminated by other sulphides, particularly those of manganese, nickel, cobalt and iron. There is also danger of zinc sulphide coming down with the lead sulphide in a very weakly acid solution, so that this precipitate should be examined for zinc.

Precipitation as Zinc Ammonium Phosphate.

Dissolve the zinc sulphide in a little dilute hydrochloric or nitric acid into a beaker and boil out the hydrogen sulphide. Nearly neutralize by ammonia; dilute to about 150 c.c. and warm on a water-bath, then add a solution of ammonium phosphate, $(NH_4)_2HPO_4$, containing ten times as much as is required

to combine with the zinc. If the precipitate does not form, add ammonia carefully until it separates. Warm on the water-bath until the flocculent precipitate changes completely to the crystalline, $ZnNH_4PO_4$; continue heating for fifteen minutes longer, allow to cool and filter. The precipitate may be treated in a variety of ways, but it is best to weigh as $ZnNH_4PO_4$, after drying at 100–105° C., rather than to ignite to pyrophosphate. Filter on paper, wash with a 1 per cent. ammonium phosphate solution, then with dilute alcohol. Dissolve the precipitate through into a weighed platinum dish by dilute nitric acid; evaporate to dryness and weigh as $ZnNH_4PO_4$ after drying at 100°–105° (this phosphate has no water of crystallization); or filter on a Gooch crucible, using asbestos, or on balanced filters, as already described. The precipitate is readily soluble in acids or ammonia, and slightly soluble in very large quantities of ammonium salts, especially when hot. Microcosmic salt can be used with ammonium chloride not exceeding 20 grams.

Notes. — The important properties have been given. Any other metal except alkali will cause contamination. On ignition to pyrophosphate, extraordinary care is required to avoid volatilization of zinc. The two points to be observed are a large excess of reagent to get a sufficiently complete precipitation (solubility product large) and sufficient concentration of NH_4 ions to change the flocculent precipitate completely to $ZnNH_4PO_4$. As the $(NH_4)_2HPO_4$ gives both and the excess is easily washed out, it is the preferable reagent.

Modified Waring Method.*

After decomposing the weighed sample by acids alone or aided by fusion as the case may require, all the zinc is to be brought into solution as sulphate. If nitric acid was used in the decomposition, all traces of it must be expelled by evaporation with hydrochloric and sulphuric acids successively or by two evaporations with sulphuric acid, finally to abundant evolution of fumes of sulphur trioxide. Dissolve the mass in 25 to 40 c.c. of water, add sufficient sulphuric acid to bring the free acid in the solution up to 10 or 15 per cent. Introduce a piece of heavy sheet aluminum and boil 10

* Recommended by Sub-committee on Zinc Ore Analysis of the American Chemical Society, *Jour. Amer. Chem. Soc.*, 29, 265.

minutes, or to complete reduction. Filter and wash through a filter containing a piece of aluminum into a beaker containing a stirring rod or strip of the same metal, cool, add a drop of methyl orange and neutralize carefully with sodium bicarbonate to a light straw color. Add, drop-wise, dilute formic acid (20 per cent. strength) until the pink color is just restored, then 5 drops more. (Dilute hydrochloric acid, one part strong acid to 6 parts water, may be substituted for formic acid when ammonium sulphocyanate * is to be introduced.) Dilute to about 100 c.c. for each 0.1 gram Zn possibly present, add, if much iron is present, 2 to 4 grams ammonium sulphocyanate, remove the strip of aluminum, heat nearly to boiling and saturate with hydrogen sulphide. Allow the pure white zinc sulphide to subside for a few minutes, then filter and wash with hot water. Transfer precipitate and filter to a capacious beaker, heat with 8 or 10 c.c. of strong hydrochloric acid and 30 or 40 c.c. of water until the zinc is all in solution. Determine the zinc as pyrophosphate, containing 42.91 per cent. zinc; or by titration with ferrocyanide. The use of ammonium heptamolybdate † in one per cent. solution as an indicator instead of uranium acetate or nitrate is recommended, provided all free hydrogen sulphide has been previously expelled from the solution by heating. If a blue color still appears in the test drop, add a crystal or two of sodium sulphite to the zinc solution, to decompose any remaining hydrogen sulphide.

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CHAPTER X.

Limestone Analysis.

The determinations usually required are silica, alumina and ferric oxide (together), lime, and magnesia. When a complete analysis is desired carbon dioxide, water, manganese, phosphoric acid, sulphur and organic matter must be determined and sometimes also barium, strontium, chlorine, fluorine, potassium and sodium. Whatever may be required, the most important determinations are the first four, as these indicate the composition with sufficient exactness when the limestone is used as a flux in a blast furnace. For this purpose the determination of sulphur and phosphorus may also be needed.

As this "limestone" analysis is important also for rocks, clays, cement, water for boilers, etc., it will be given in considerable detail.

* SCHEME IN OUTLINE.

Dissolve one gram in 5 c.c. conc. HCl, 1 c.c. conc. HNO_3 and 20 c.c. water with heat in a small casserole, filter.

Residue.	*Filtrate.*
Fuse + $NaKCO_3$, dissolve in HCl and add to filtrate.	→ Evaporate to dryness and dehydrate in an air-bath, take up with H_2O and HCl, heat and filter.

Residue.	*Filtrate.*		
SiO_2, etc., weigh after igniting with blast lamp. Then drive off SiO_2 by HF. Fuse any residue with $NaKCO_3$ and if Al_2O_3 add to filtrate.	Precipitate twice by ammonia, filter, wash.		
	Ppt.— $Fe(OH)_3$, $Al(OH)_3$ ± P_2O_5, ignite and weigh.	*Filtrate.*—Precipitate twice by $(NH_4)_2C_2O_4$ in neutral solution.	
		Ppt.—CaC_2O_4, wash, ignite and weigh as CaO or $CaSO_4$, or titrate the combined oxalic acid by $KMnO_4$.	*Filtrate.*—Precipitate the Mg as $MgNH_4PO_4$, ignite and weigh as $Mg_2P_2O_7$, dissolve in HCl and reprecipitate.

This scheme is without the detail which is especially important in this analysis, and is given only to show the relation of the different parts of the analysis.

DETERMINATION OF SILICA AND OXIDES OF IRON AND ALUMINUM.

Weigh out exactly one gram of the finely ground sample, transfer it to a small beaker and treat with 20 c.c. of water, 5 c.c. of concentrated hydrochloric acid and about 1 c.c. of concentrated nitric acid, cover with a watch glass and heat until no further solution takes place. Filter through a very small paper into a small casserole and wash the residue once or twice with water. Place the filtrate and washings on the water or steam-bath to evaporate.

If the limestone contained $CaCO_3$, $MgCO_3$, $FeCO_3$ and SiO_2 only, the residue, after more careful washing, could be ignited and weighed as silica, as in this form it is insoluble in acids. This is sometimes true and saves much time with the analysis, but if there are present silicates of lime, magnesia, etc., these may be insoluble or may give gelatinous silica which dissolves partly, so to ensure accurate results it is necessary to fuse the residue to decompose some silicates and also to evaporate and dehydrate the solution to obtain the soluble silica.

The nitric acid is added to oxidize the iron which may be present as pyrites, FeS_2, or as siderite, $FeCO_3$.

While the filtrate is evaporating, dry and burn the filter containing the residue in a small platinum crucible, then add about six times its weight of mixed carbonates and a crystal of nitrate, the size of a pin head, and fuse for about 15 minutes over a Bunsen burner. The fusion should be perfectly liquid; if it is not, increase the heat or the flux or both until a complete decomposition of the insoluble residue is obtained, bearing in mind the disadvantage of introducing into the analysis large quantities of alkali salts. When cold remove the melt in a cake if possible, dissolve it in hydrochloric acid and water and add this to the solution which is evaporating on the water-bath. Continue the evaporation to dryness, stirring with a glass rod, when the salts begin to crystallize; then transfer to an air-bath and heat at 110° C. until there is no more smell of hydrochloric acid.

If the insoluble residue consisted of silicates of calcium, magnesium or aluminum after fusion there are present $CaCO_3$, $MgCO_3$, $Na_2Al_2O_4$, Na_2SiO_3 and the corresponding potassium salts; on treating with acid these give $CaCl_2$, $MgCl_2$, $AlCl_3$ and H_2SiO_3,

besides NaCl and KCl. After combining the two solutions we have $CaCl_2$, $MgCl_2$, $FeCl_3$, $AlCl_3$, H_2SiO_3, NaCl, KCl, HCl. As the calcium chloride is the predominating salt, the dehydration of the silica will be easy on account of its great affinity for water (compare action of sulphuric acid in Drown's method for silicon), so that in the analysis of an ordinary limestone it is not necessary to repeat the dehydration.

After dehydration treat the mass of salts with hydrochloric acid and water, heat to dissolve the salts of iron and aluminum and filter out the silica, which should be perfectly white. Wash with hot water, being careful to use a wash bottle which gives a very fine stream, so as not to dilute the filtrate to more than 100 c.c. Burn the paper and ignite the silica over the blast-lamp to drive off the last of the water, cool in a desiccator and weigh. Check this by driving off the silica by hydrofluoric and sulphuric acids as already described under iron ore. If there should be a residue it is probably alumina, in any event fuse it with a little mixed carbonate, dissolve the melt in hydrochloric acid and add this to the filtrate from the silica.

To the main filtrate add ammonia in slight excess, and heat to boiling, so that the flocculent precipitate of ferric and aluminum hydroxides collects well. This contains any phosphoric acid present and is probably contaminated by calcium and magnesium hydroxides. Allow to settle, and decant through a filter, leaving all of the precipitate in the bottom of the beaker. Dissolve the precipitate in dilute hydrochloric acid and reprecipitate by ammonia, heat again, filter and wash till free from chlorides by boiling water, avoiding unnecessary dilution of the filtrate. Filter without delay as the alkaline solution will absorb carbon dioxide from the air and so cause contamination due to calcium carbonate. The remedy would be to redissolve in acid, boil out the carbon dioxide and reprecipitate. Burn the paper, etc., moisten the residue with nitric acid and ignite finally by the blast-lamp and weigh the combined oxides of iron and aluminum.

Precipitation of Calcium Oxalate.

The filtrate, containing $CaCl_2$, $MgCl_2$, KCl, NaCl, NH_4Cl, etc., is made decidedly acid with hydrochloric acid; then enough oxalic

acid is added to combine with all the lime and the solution is heated to boiling.

To the boiling solution a few drops of methyl-orange are added and then gradually and with frequent pauses dilute ammonia, till the indicator changes color. The neutralization should take half an hour, then a considerable excess of ammonium oxalate is added and the precipitate allowed to stand for four hours. Next filter and wash with a 1 per cent. solution of ammonium oxalate.* Although if these conditions are carried out very carefully it is possible to obtain a very complete separation of calcium from magnesium by one precipitation, it is safer to redissolve the precipitate in hydrochloric acid, after decanting or filtering, and to reprecipitate as before by neutralizing with ammonia and then adding ammonium oxalate.

The main difficulty in precipitating calcium oxalate is the contamination due to magnesium oxalate. Although this is a perfectly soluble salt it is carried down by the calcium oxalate (adsorption) and not readily removed by washing. An alkaline solution is most favorable to this contamination; so, if to the acid solution we add enough oxalic acid to combine with the lime and then neutralize gradually, the calcium oxalate will be formed in as acid a solution as possible and also in one in which it is somewhat soluble, hence it will be free from magnesium oxalate and also in large crystals which can be easily filtered and washed. The indicator, methyl-orange, turns before an excess of ammonia has been added. If we stopped at this point we would not get complete precipitation of the calcium as there is not yet present any considerable excess of ammonium oxalate, so then an excess of ammonium oxalate is added, which converts the magnesium largely to oxalate, and by the mass action of the C_2O_4 ions the solubility product of calcium oxalate is exceeded, the Ca ions are driven out of solution, and the precipitation of the calcium oxalate is complete. Now that the magnesium is present largely as oxalate, we must not wait too long before filtering, as it has been found that the magnesium oxalate increases on the precipitated calcium oxalate. As the calcium oxalate is very slightly soluble in hot water, it is washed with a solution containing an ion in common, 1 per cent. ammonium oxalate.

* Richards, *Zeits. anorg. Chem.*, **28**, 88.

If the calcium is to be determined gravimetrically, the ammonium oxalate need not be removed; if a volumetric method (potassium permanganate) is to be used this must be washed out with cold water.

When calcium oxalate is ignited it gives a mixture of carbonate and oxide; this can be heated by a blast-lamp for half an hour or more until constant weight is obtained and the resulting calcium oxide weighed. Great care must be observed to expel all the carbon dioxide and to avoid any reabsorption of this or of water from the air, by using a crucible with well-fitting cover and cooling in a desiccator and weighing quickly.

After burning the paper, etc., the residue can be converted to sulphate by moistening with dilute sulphuric acid and heating carefully over a Bunsen burner (no blast) till the excess is expelled, then weighing when cold and repeating the treatment until a constant weight is obtained.

When the oxalic acid combined with the calcium is to be titrated by permanganate, proceed as follows: Dissolve the precipitate through the filter with the least possible quantity of hot dilute hydrochloric acid into a large beaker, dilute with warm water, add an excess of concentrated sulphuric acid (5–6 c.c.), ten grams of manganous sulphate, and titrate at about 65° C. Or dissolve through the paper in very dilute sulphuric acid, add more sulphuric acid, warm and titrate.

Besides the properties of calcium oxalate already mentioned, like barium sulphate, when formed in a cold solution, it is very fine and runs through the filter. It is dissolved by mineral acids and is slightly soluble in acetic acid. It should be precipitated in a solution containing no salts other than those of magnesium and the alkalies, as it would be contaminated by barium oxalate, manganous oxalate, etc.

Magnesium Determination.

The filtrate should be about 200 c.c. in volume, and will contain a large amount of ammonium chloride and oxalate. If the amount of magnesium is considerable (dolomite) it can be precipitated in this solution by adding sodium or ammonium phosphate and then an excess of ammonia, etc., as already explained. After igniting and weighing the magnesium pyrophosphate, it is best to dissolve

it in dilute hydrochloric acid and to weigh any residue of silica with the crucible. Then subtract this weight instead of the original weight of the crucible, as the ammonia salts are likely to cause contamination of the precipitate by silica from the beakers.

If the amount of magnesia is small, as is usually the case, it will not come down satisfactorily in the presence of the relatively large amounts of ammonia salts. Concentrate the solution as far as possible in a beaker, then transfer to a platinum dish and evaporate to dryness. If the salts crawl up the sides, heat the upper edge of the dish instead of the bottom, best by putting a top on the burner which gives a number of small flames from the sides. Then ignite to drive off the ammonia salts, take up the residue with dilute hydrochloric acid, filter if necessary (to remove dust and silica) and determine the magnesia as usual.

A very good method of getting rid of ammonium chloride is to add to the very concentrated solution in a casserole (just as the salts are beginning to separate) strong nitric acid and continue the evaporation. The ammonium chloride breaks up and is expelled, probably according to the following reaction :

$$NH_4Cl + HNO_3 = HCl + 2H_2O + N_2O,$$

while the excess of nitric acid helps to decompose the oxalates.

When the oxalates are not destroyed and sodium phosphate is used as a precipitant, the magnesium ammonium phosphate must be washed very thoroughly to remove the sodium oxalate.

Effect of Barium, Manganese or Phosphoric Acid.

If the limestone contained a little barium carbonate and considerable pyrites, barium sulphate would be formed, which would contaminate the silica. After driving off the silica, fuse the residue as usual and, if a precipitate is reformed on acidifying, filter and add only the clear solution to the main filtrate. It might happen that the barium carbonate was in excess of the sulphur, so that only a portion would be precipitated as barium sulphate while some would come down as oxalate and the rest as phosphate. In such a case add dilute sulphuric acid drop by drop before filtering off the silica so as to precipitate all the barium, avoiding much excess, so as not to form calcium sulphate which would contaminate it.

Then, after driving off the silica, the barium sulphate can be weighed if pure or fused and reprecipitated.

Should there be *manganese* present it will contaminate the ammonia precipitate unless the precipitation is repeated, and also the calcium oxalate. It is possible to precipitate calcium as oxalate in the presence of iron but not in that of manganese (see slag analysis) so that the manganese must be removed before the precipitation of calcium oxalate. This can be done as follows:

1. After several ammonia precipitations add bromine water and ammonia, warm and filter out the higher hydrated oxide of manganese.

2. Saturate the filtrate, slightly alkaline with ammonia, with hydrogen sulphide and filter out the manganous sulphide.

3. Substitute the basic acetate for the ammonia precipitation and take the manganese out of the filtrate by either bromine or by hydrogen sulphide.

The determination of manganese has been described.

There are cases in which the amount of *phosphoric acid* is more than enough to combine with the iron or iron and aluminum present, so that the ammonia precipitate will also contain calcium as phosphate, which can not be removed by solution and reprecipitation. In such a case add a known amount of iron as ferric chloride, which shall furnish an excess over that required to combine with the phosphoric acid, and precipitate with ammonia as usual. All the lime will be in the filtrate and the ferric oxide from the iron solution added must be subtracted from the weight of the total alumina and ferric oxide.

Applications of the "Limestone" Analysis.

The most important variations when this analysis is to be applied to a *rock* are:

1. Fuse the entire rock with Na_2CO_3 or $NaKCO_3$, because so little will dissolve in acid that the treatment is not advisable.

2. Dehydrate the silica by evaporation on a water-bath twice, or if very high in silica (acid rock), three times. The reason for this is seen when we compare the composition of limestone with that of rock. Limestone contains perhaps 2–3 per cent. of silica and 45–50 per cent. of lime. Rock, 60 per cent. or even 80 per

cent. of silica and a small amount of lime. So that if one hundredth of the silica present escapes the first dehydration, the error is 0.6–0.8 per cent.

3. Always look for manganese in a rock, a green fusion due to manganate when nitrate is added to the mixed carbonates in the fusion, but not always formed without the nitrate.

With *clays* the treatment is similar to that given for rocks, but here the percentage of alumina is higher and that of lime and magnesia lower, so that the double dehydration of the silica is necessary, and also the refusion of any residue left after driving off the silica, which will usually be alumina, possibly also titanic oxide. The aluminum and ferric hydroxides must be very carefully precipitated in the presence of ammonium chloride and with but a slight excess of ammonia.

With rock, clay or cement, it is not enough to obtain the combined per cent. of Al_2O_3 and Fe_2O_3; the iron, ferrous or ferric, is also required. This can be done as follows: After igniting and weighing the combined oxides, fuse them for at least forty-five minutes at a low heat with 8–10 times their weight of potassium bisulphate or potassium pyrosulphate, then at the end add concentrated sulphuric acid to reconvert the potassium sulphate to bisulphate. This changes the iron and aluminum to sulphates and at the same time dehydrates any silica which has previously escaped and has precipitated with the hydroxides. Dissolve the melt in water and sulphuric acid, filter, add the silica to the main portion, reduce the iron in the filtrate by passing it through a reductor and titrate by permanganate.

For cements, which often contain about 22 per cent. of silica and 60 per cent. of lime, two evaporations for silica, and the separate percentages of oxides of iron and aluminum, constitute the important variations from the "limestone" analysis described.

For the best information on limestone and rock analysis see Hillebrand, *Bulletin of the U. S. Geological Survey*, No. 305. For cement analysis, report of committee, *Jour. Soc. Chem. Ind.*, **21**, pp. 12–30, and Hillebrand, *Jour. Amer. Chem. Soc.*, **25**, 1180.

This discussion also covers the main portion of slag analysis; the composition of slag varies within wide limits, and there may be present any of the common or rare elements. But bearing in

mind that the fifth and sixth groups are taken out after the silica, and the principles of the "limestone" analysis, the special methods given later for typical slags will easily be understood.

Determinations of Carbon Dioxide, Sulphur and Phosphorus.

The other determinations in limestone are made in separate portions.

Carbon dioxide is either found by loss or by direct weight, the methods are given in the text-books.* A rapid method is to fuse about four grams of borax glass ($Na_2B_4O_7$) in a platinum crucible, and when cold weigh; place about one gram of the dried limestone on the top of the borax glass and reweigh. Then fuse with a Bunsen burner (no blast) till no more gas is given off, cool and weigh. The loss in weight is carbon dioxide, provided there is no moisture or organic matter present. The method is only approximate, as borax glass is slightly volatile and gives total carbon dioxide, water and organic matter, when the latter are present.

The reaction is $Na_2B_4O_7 + CaCO_3 = Na_2B_2O_4 + CaB_2O_4 + CO_2$.

Sulphur. — Unless barium sulphate is present, dissolve five grams of a sample in 15 c.c. concentrated hydrochloric acid and 5 c.c. concentrated nitric acid and 15 c.c. of water in a casserole, evaporate, add more hydrochloric acid and evaporate to dryness to expel the nitric acid and dehydrate the silica; take up with hydrochloric acid and water, boil and filter; neutralize the filtrate with ammonia so that it is just acid with hydrochloric and precipitate the sulphate by barium chloride as usual.

If barium sulphate is present, fuse the residue with mixed carbonates, leach with water, filter out the barium carbonate and add the filtrate to the main solution, dehydrate and precipitate as usual.

Phosphorus. — Dissolve 5 grams in 40 c.c. of dilute nitric acid, evaporate to dryness, take up with nitric acid and water, filter, neutralize the excess of nitric acid by ammonia, and precipitate as ammonium phosphomolybdate, etc., as in iron ore. If the iron and alumina are low, the molybdate precipitation can be omitted. Dissolve 5 grams in hydrochloric acid, evaporate, bake, take up with

* Cairns' "Quantitative Analysis," pp. 33–37.

hydrochloric acid and water, filter; to the filtrate add 2–3 grams of citric acid, to prevent the precipitation of aluminum or ferric hydroxides or calcium phosphate, neutralize with ammonia and precipitate by magnesia mixture direct.

Sulphur and phosphorus are objectionable when the limestone is used as a flux for iron ores.

CHAPTER XI.

The Determination of Copper in Ores and Mattes.

Among the many methods which have been proposed for the determination of copper the electrolytic, iodide and cyanide are of the greatest importance and the thiocyanate and colorimetric methods deserve mention.

As the *method of solution* is the same for all these methods, it will be described first.

For ores, weigh out, depending on the richness, from 1 to 5 grams of the very finely ground sample, so as to obtain about 150 milligrams of copper. Treat this in a covered casserole or Erlenmeyer flask (200 c.c.) with 20 c.c. concentrated nitric acid, 5 c.c. concentrated hydrochloric acid and 5 c.c. concentrated sulphuric acid; heat until all the copper has dissolved and then evaporate to dense white fumes of SO_3 (at this point the blue color will have disappeared, no water being present), allow to cool; dilute with water and heat to dissolve ferric sulphate, etc.; filter out the residue, which consists of silica, silicates and the insoluble sulphates of lead, barium, etc., wash this residue with hot water thoroughly, taking care to avoid unnecessary dilution.

This treatment will dissolve the copper in all ordinary ores, but if it is present as silicate (chrysocolla or slags) the residue should be fused with mixed carbonates to ensure complete decomposition.

For mattes, use 0.25–0.5 gram and half the quantities of nitric and hydrochloric acids and about 4 c.c. of sulphuric acid. Alloys such as brass, german silver, etc., can be treated in the same way when it is desired to separate out the lead as sulphate; or dissolved in nitric acid alone, depending on the methods to be used for the subsequent separations. With bronze nitric acid alone is used followed by long boiling in a very dilute solution, so as to separate out the tin as completely as possible, as metastannic acid. This often contains copper which is separated from tin by digesting the residue on a water-bath with potassium sulphide (not am-

monium sulphide). This also applies to brass and german silver when they contain tin.

Electrolytic Method.

The sulphuric acid solution containing $CuSO_4$,$Fe_2(SO_4)_3$, etc., besides the possible impurities, arsenic, antimony, bismuth, can be electrolyzed directly, provided there is not too great an excess of sulphuric acid present; 2–3 c.c. of concentrated acid in a volume of about 100 c.c. is a suitable quantity; if this is exceeded a portion can be neutralized by ammonia. If the copper is from a chalcopyrite there will be a considerable quantity of ferric sulphate present, and the separation of copper succeeds best under the conditions given. It is impracticable to precipitate the iron by ammonia before electrolysis as the ferric hydroxide always carries down copper. If difficulty is encountered in depositing the last traces of copper, the solution after electrolysis can be made alkaline by ammonia and when there are only traces of copper present, the amount held by the precipitate can be neglected. In the filtrate the copper can be determined colorimetrically or the solution made acid again by sulphuric acid and the electrolysis continued.

The colorimetric estimation consists in comparing the shade of blue in the ammoniacal solution with the color of standards made up containing known amounts of copper in the same volume and having the same excess of ammonia and at the same temperature. For the details of this method see Heath, *Jour. Amer. Chem. Soc.*, **19**, 24, and Smith, *Trans. Amer. Inst. M. E.*, **30**, 851, 1901. When arsenic and antimony are present in large quantities, the method described, or any other electrolytic method, fails to give accurate results, as some of these impurities are deposited with the copper. This may be remedied by roasting the material before dissolving (after weighing), or by repeated evaporations with bromine, or by heating the precipitated sulphides with a solution of sodium or potassium sulphide, filtering and then dissolving the copper sulphide in nitric acid.

When the arsenic and antimony are present only in exceedingly small quantities the presence of nitric acid prevents or retards their deposition, so that the best conditions for the electrolysis of a copper matte are, as regards acidity, 2–3 c.c. of sulphuric acid 1.84 sp. gr. and 2 c.c. nitric acid 1.42 sp. gr. in a volume of about 150 c.c.

Bismuth is the most troublesome metal in connection with all the methods for copper; it is not removed by roasting, and although not easily precipitated completely by the current, it always contaminates the copper when present, often without causing any perceptible discoloration of the deposit. If present, dissolve the deposited copper in nitric acid, add ammonia in excess, then ammonium carbonate, dilute to 150 c.c. and boil. The bismuth is precipitated as a basic carbonate, contaminated by copper; by resolution in nitric acid and reprecipitation it can be obtained pure; then washed, ignited and weighed as Bi_2O_3. The calculated weight of bismuth is deducted from the weight of the deposit.

When the bismuth is present in large amount, or when it is also to be determined, the method described by Riederer, *Jour. Amer. Chem. Soc.*, **25**, 919, 1903, can be employed.

The special apparatus required for the determination of copper consists of platinum electrodes and a suitable stand.

The anode is usually made of a stout platinum wire, bent into a spiral when a cylindrical cathode is used or coiled into a disc when a platinum dish is used. The cylindrical cathode is most convenient when many determinations are made at the same time; it should be open at the side so as to allow the circulation of the electrolyte. Both electrodes should be thoroughly clean, free from deposited metal, grease or dust. This is obtained by treatment with nitric acid and then drying above the flame of a burner.

The cathode is then weighed and connected with the negative pole of the battery or source of electricity, while the anode is connected with the positive pole. With cylindrical electrodes the copper solution is placed in a small but tall beaker and the cathode adjusted so that about half an inch is out of the liquid, and the beaker covered by a divided watch glass to keep out dust and prevent loss by spattering.

The area of the cathode should be about ten square inches and the current 1.5–2 volts and 0.1–0.2 ampere. It is turned on and the copper allowed to deposit for from twelve to fifteen hours, then if the electrolyte is colorless the cathode is lowered about one fourth inch so as to expose a fresh surface of platinum for deposition and the electrolysis is continued for an hour longer. When no more copper is deposited, a few c.c. of the solution are with-

drawn by a pipette and tested with freshly prepared hydrogen sulphide water on a white surface. This test is much more delicate than the blue color with ammonia.

As there is nitric acid present the cathode must be removed while the current is still passing, otherwise the nitric acid would immediately begin to redissolve copper. This can be done by siphoning out the contents of the dish and at the same time adding water, until the solution is too dilute to attack the deposit, or if the electrolysis is done in a beaker, the block beneath it can be removed and a beaker of water substituted, then the cathode is allowed to drop into the water.

The deposited copper must be dried without oxidation; so it is next rinsed off with alcohol to displace the water, then, when great precautions are required, with ether and is dried at a very gentle heat — such as can easily be borne by the hand — so as not to oxidize the deposit. When cold it is allowed to stand in the balance room for about ten minutes and then weighed.

For the electrolytic assay as applied to refined copper, see Heath, *Trans. Amer. Inst. M. E.*, July, 1899.

The behavior of the elements likely to be present, under the conditions given is briefly as follows: Iron does not interfere unless insufficient sulphuric acid is present. Then the nitric acid becomes reduced to ammonia, which precipitates ferric hydroxide. In the directions given, the amount of sulphuric acid is sufficient to neutralize all the ammonia formed, even if the nitric acid is completely reduced.

Nickel and cobalt do not interfere in a strongly acid solution. They are, however, deposited in an ammoniacal solution, if the current is strong. Zinc requires the presence of a strong acid to prevent its precipitation, *i. e.*, nitric; it may be deposited in an extremely weak sulphuric acid solution or readily from solutions of organic acids, like acetic, citric, lactic, etc. So that if the electrolysis is prolonged and the free nitric acid reduced zinc may be deposited. Manganese does not deposit as metal, but goes to the anode as peroxide; it is sometimes oxidized higher to permanganic acid which gives a color to the solution about the anode. Lead in traces escapes precipitation as sulphate and appears on the anode as PbO_2. Bismuth contaminates the copper

and also goes to the anode as peroxide. Arsenic and antimony are liable to contaminate the copper as explained.

Silver will be removed as chloride, unless the digestion with concentrated sulphuric acid is very long, then it is partly changed to sulphate. If present, it will deposit completely with the copper; but is easily removed by a drop of a chloride. Gold, platinum, etc., would be deposited, but are not likely to be present in sufficient quantity to influence the results.

In general salts are objectionable, although in some cases they are added. For example, Classen precipitates copper and other metals from a solution containing large amounts of ammonium oxalate. Hydrochloric acid and chlorides should be absent, as they cause the deposit to be spongy.

For a detailed discussion of the quantitative deposition of metals by electrolysis see "Electrochemical Analysis," by Prof. E. F. Smith, 1902.

It is of the greatest importance that a dense firmly adherent deposit be obtained, free from impurities; aside from the chemical conditions, the character of the current has much influence on that of the deposit.

To describe the current we must know the voltage and amperage; the latter is often given as current density, that is, the number of amperes per 100 sq. cm. of cathode area. ND.100 = 0.2 means 0.2 ampere for each 100 sq. cm. of the submerged area of the cathode on which metal is deposited.

The amperes determine the rate of deposit, according to Faraday's law, but in quantitative analysis the character is of greater importance than the rate, so for copper a low-current density is used, 0.1–0.2 ampere, because a stronger current (except in special cases) is liable to give a dark, spongy and non-adherent deposit, which is difficult to dry without oxidation, and to weigh without loss.

The voltage should also be high enough to overcome the counter-electromotive force of the solution and its resistance, for copper about 1.5 volts; but not much higher as a high voltage tends to increase the impurity of the deposit. The best current for electrolytic work can be obtained from storage batteries, or primary batteries; but as the lighting circuits are more convenient, they may be used by inserting a suitable resistance.

The counter-electromotive force necessary to deposit a metal can be calculated from the heat of formation of the molecule, and the results so obtained agree well with those found by experiment. But the question may well be asked, if salts, such as copper sulphate, are already ionized in solution, why is all this energy required to pull the copper sulphate apart? The answer is found in Nernst's solution-tension theory. This is, briefly that each metal has a certain power of forcing its atoms into solution as ions; just as a liquid continues to evaporate at its surface till the pressure of the vapor becomes equal to the vapor-tension of the liquid, so the metal sends ions into solution till the osmotic pressure of these ions becomes equal to the solution-tension of the metal. Therefore, in order to separate out the copper ions in the form of metallic copper, a certain electrical pressure or intensity of current is required, so that the sum of this and the osmotic pressure shall exceed the solution tension.

These differences in solution tension for different ions can be found in the books on physical chemistry, and while the results agree well with the old method of calculating counter-electromotive force, the modern method is more accurate, as it considers the variation of voltage with dilution.

There is therefore a minimum voltage below which any given metal will not be deposited, so that theoretically, if all metals gave soluble sulphates or nitrates, we could apply just voltage enough to overcome the solution tension of the lowest in the series and when that metal was completely deposited, the current would cease to pass; then by raising the current to just above the intensity required for the next metal, that could be deposited and so on. This is evidently not possible in all cases, but it is in some. If there are present in solution copper and silver as nitrates and a current of one volt is passed, only silver is thrown out. If the sulphates of copper and zinc are in solution (containing but a trace of free sulphuric acid) we can by keeping the current between 1.5 and 2 volts deposit only copper; while by raising the voltage so as to exceed the solution tension of the zinc, we can deposit brass and by varying the voltage, vary the percentage composition of the alloy.

To return to the copper, we can prevent some metals from de-

positing by the character of the solution, addition of acid, etc., others will not come down in an aqueous solution at all, others can be prevented from contaminating the copper by regulating the voltage so that the counter-electromotive force of copper is just exceeded. Practically it is often easier to remove the interfering element than to regulate the voltage, and then, when there is no metal present which will come down at a higher voltage, we need only adjust the amperage or current density so as to get a deposit suitable for weighing.

Additional References.

"The Elements of Electrochemistry," by LeBlanc, translated by W. R. Whitney for the theory, and "Quantitative Chemical Analysis by Electrolysis" by Classen for other methods.

Iodide Method.

In an acetic acid solution, potassium iodide precipitates cuprous iodide, with the liberation of iodine, according to the reaction:

$$2Cu(C_2H_3O_2)_2 + 4KI = Cu_2I_2 + I_2 + 4KC_2H_3O_2,$$

or one atom of iodine is liberated for each atom of copper present in the cupric condition.

The liberated iodine can be titrated by a standard solution of sodium thiosulphate, using starch solution as indicator, according to the reaction:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

Here copper acts as an oxidizing agent, liberating iodine, which is measured, and so the copper is determined; a method of indirect titration. It is evidently essential to the success of this method that there should not be present any other oxidizing or reducing agents, for the first would liberate iodine and cause too high results; the latter would be oxidized by the iodine liberated and cause too low results.

The *indicator* is a solution of starch which gives an intense blue color to the solution in the presence of free iodine. The end point is the discharge of this blue color and is extremely delicate when the proper conditions have been observed. The starch solution is

made by mixing about one gram of pure starch to a thin paste with cold water and then pouring it into about 200 c.c. of boiling water and boiling for several minutes. It should be allowed to cool and only the clear solution used. This solution does not keep well. Moulds grow in it which split up the starch giving other carbohydrates, some of which give reddish colors with iodine. To guard against this a preservative such as zinc chloride or carbon bisulphide may be added.

A *standard solution of sodium thiosulphate* is made by dissolving 19.6 grams of the crystallized salt, $Na_2S_2O_3.5H_2O$, in water and diluting to one liter. Each c.c. will be equivalent to about 5 milligrams of copper. Standardize as follows: Weigh out two or three portions of pure bright copper foil of 100–150 milligrams each, taking different weights, as this ensures a really independent determination and saves the time required to weigh out an exact amount. Dissolve the copper in small beakers in about 10 c.c. or less of nitric acid 1.2 sp. gr., evaporate until all red fumes and all excess of nitric acid are expelled, best on a steam-bath; redissolve the copper nitrate in a little water, add a few drops of sodium hydroxide, which should give a slight precipitate of cupric hydroxide, dissolve this in a few c.c. of acetic acid, allow to cool and dilute with cold water to about 50 c.c.

Next add three grams of potassium iodide crystals (or in solution), stirring until they have dissolved. The solution now contains a precipitate of almost white cuprous iodide and is colored brown by the liberated iodine. Run in the sodium thiosulphate solution from a burette until the brown color is very faint, a light straw color, then add about 5 c.c. of the clear starch solution and continue the titration until the blue is discharged. Near the end the sodium thiosulphate must be run in drop by drop and the solution stirred thoroughly. Titrate the other portions and calculate the value of the solution in terms of copper. The standards should not differ by more than one in the fifth decimal place (third significant figure).

The blue color will return after a time due to oxidation by the air. If the solution remains colorless for two minutes the end has been reached and the titration is satisfactory. If the blue reappears almost immediately there is probably some oxidizing agent

present and if this continues after the addition of a couple more drops of thiosulphate solution the determination is useless.

After the potassium iodide has been added the solution must be kept cold to avoid loss of iodine and titrated without delay to avoid oxidation by the air. As large amounts of sodium acetate interfere with the end point, by causing a return of the blue color, care should be taken to add only a few drops of sodium hydroxide solution (not carbonate) in neutralizing the nitric acid.

Assay. — To the sulphate solution of the ore or matte add two pieces of sheet aluminum, one sixteenth inch thick and one and one half inches square, whose corners are bent so that the two pieces touch only at the points and so present a large surface, then about 5 c.c. of strong sulphuric acid. Heat to boiling, covered to prevent spattering, until all the copper is precipitated. Pour the solution and that portion of the copper which does not adhere to the aluminum foil into a clean beaker and allow the copper to settle; then decant through a filter, wash with water the aluminum foil coated with copper, and the loose copper in the second beaker, pour the washings through the same filter; remove the vessel containing the filtrate and washings and substitute the other beaker containing the non-adherent copper; to the beaker containing the aluminum foil add 5–6 c.c. of nitric acid 1.2 sp. gr. and warm till all the copper has dissolved, then pour the acid copper nitrate solution through the filter into the beaker below, which contains the rest of the copper, wash, and heat till all the copper has dissolved.

If the precipitated copper is red in color and evidently pure, the washings of the beakers and filter can be added at once and the excess of nitric acid expelled and the copper titrated exactly as in standardizing. If the copper is dark, before diluting with the washings add half a gram of potassium or sodium chlorate or one half c.c. bromine and boil to oxidize any arsenic which may be deposited with the copper, then add the washings and evaporate as usual. When antimony is present it will be oxidized by the nitric acid and be almost all filtered out; the traces which dissolve must be oxidized like the arsenic. It is of the utmost importance that all the chlorate is decomposed and the chlorine and oxides of chlorine boiled out, as these would liberate iodine later on.

Bismuth will be deposited with the copper by the aluminum, it

will dissolve in nitric acid and unless thrown out as a basic salt when the copper nitrate is dissolved in water, will precipitate as a brown iodide, BiI_3. As this is not attended by any liberation of iodine it will not affect the results, but as this iodide is somewhat soluble in potassium iodide a brown-colored solution is produced, which may look like liberated iodine, and so too much thiosulphate solution may be run in before the starch solution is added.

In titrating some ores the end point may not be exactly the same as with pure copper, due to impurities, such as bismuth, lead, etc., which give a greenish solution after the starch is added so that the change is not from blue to white, but from a dirty green to a yellowish white.

The amount of potassium iodide has been given as three grams; this quantity is required for the reaction and the excess necessary to hold the liberated iodine in solution. More does no harm, but as the reagent is expensive, it should be used sparingly. The end point is so sharp that slight variations of the volume or of the amount of copper present have no effect. Ferric salts can not be present, as they liberate iodine; in the method described they are reduced to the ferrous condition when the copper is precipitated by aluminum and are thrown away in the filtrate. If sodium carbonate is used instead of hydroxide in neutralizing the copper nitrate solution some copper remains in solution as bicarbonate. Then, when the potassium iodide is added, iodine and carbon dioxide are liberated together, and some iodine is lost by being carried out with the carbon dioxide.

It has been proposed recently by Low to neutralize here with ammonia and then to acidify by acetic acid as described; also to oxidize any arsenic or antimony present to the pentad condition by bromine instead of chlorate. For further information on this method see: Low, *Jour. Amer. Chem. Soc.*, **18**, 458 and **24**, 1082. Beringer's "Assaying," p. 160.

Potassium Cyanide Method.

This method is very largely used, as it is more rapid and less expensive than the iodide method. It depends on the conversion of the intensely blue $Cu(NH_3)_4$ ion into a colorless $Cu(CN)_2$ ion, or practically the measurement of the amount of potassium cyanide

solution necessary to decolorize the ammoniacal solution of copper nitrate or sulphate.

The reaction for the sulphate is given by Treadwell as follows:

$$2Cu(NH_3)_4SO_4.H_2O + 4KCN = 2Cu(CN)_2 + 8NH_3 + 2K_2SO_4,$$

then the $2Cu(CN)_2$ breaks up, giving $Cu_2(CN)_2$ and $(CN)_2$, and, if sufficient potassium cyanide is present, forms $K_4Cu_2(CN)_6$, while the $(CN)_2$ reacts on the excess of ammonia, like Cl on KOH, giving NH_4CN and NH_4CNO. So the complete reaction is,

$$2Cu(NH_3)_4SO_4.H_2O + 8KCN = K_4Cu(CN)_6 + NH_4CN + NH_4CNO + 6NH_3 + 2K_2SO_4.$$

This is not advanced as a perfect explanation of what takes place, but to show how complex the simplest form of the reaction is. Then if we begin to consider the influence of other salts present and the easy conversion of ammonium cyanate into urea, a large field of possible organic compounds is opened; so it is evident that the reaction must be carried out under identical conditions in order to obtain accurate results. The following facts also emphasize this:

1. Increase of temperature decreases the intensity of the blue color.

2. A large excess of free ammonia tends to vary the color and give low results.

3. Ammonium sulphate gives low results.

4. Hydroxides, bicarbonates, sulphites and nitrites affect the results.

5. Salts of silver, zinc, nickel, etc., which react with potassium cyanide must be absent.

6. Ferric or manganese hydroxides should not be present, as they hold copper and mar the end point.

The titration must therefore be made in the absence of iron, manganese, zinc, nickel or silver salts, best without ammonia salts, at the same temperature (the lower the sharper the end point), with the same excess of ammonia, with the same volume at the end, and with approximately the same amount of copper present.

Make up a solution containing 22 grams of pure potassium

cyanide per liter. Weigh out two or three portions of pure copper about 150 milligrams each; dissolve them in nitric acid, in a beaker capable of holding 200 c.c. easily, with a mark at 150 c.c.; boil out the oxides of nitrogen; dilute with cold water to about 80 c.c.; neutralize with dilute caustic soda solution till a faint permanent precipitate forms; then add 6 c.c. of strong ammonia (0.9 sp. gr.) and run in the potassium cyanide solution till the blue color is very faint; dilute to the mark (150 c.c.) and continue the titration until the solution is colorless.

To apply the method to ores, etc., follow the directions given for the iodide method until the copper is precipitated on aluminum foil, dissolve this in nitric acid and proceed as in standardizing.

The method is very accurate after a little experience with the end point, and its most important feature is the necessity of absolute uniformity in the conditions of titration. Should great rapidity be required at the expense of accuracy, the ore can be dissolved in nitric acid, an excess of ammonia added, then titrated to a faint blue, the residue ferric hydroxide, etc., filtered out, and the titration finished on the clear filtrate.

The cyanide solution keeps best in the dark, but as it is constantly losing hydrocyanic acid it requires frequent standardizing.

For further information see Beringer's "Assaying," p. 154, and H. H. Miller, *Trans. Amer. Inst. M. E.*, Nov., 1901.

Thiocyanate Method.

This method has many modifications and is only recommended for low grade, impure ores or tailings containing less than three per cent. of copper and particularly when the impurities are arsenic and antimony. What follows is taken largely from an article by Guess,* and the thesis of Lindeman, Columbia University, 1903.

The essential features of the method are as follows, the preliminary treatment being as already given: The filtrate containing sulphates is neutralized by ammonia and then rendered acid by either hydrochloric or sulphuric acid (1 per cent. of either is sufficient acidity); next a slight excess of sulphurous acid is added and the solution heated, then a decided excess of potassium thiocyanate †

* *Jour. Amer. Chem. Soc.*, **24**, 708.

† Often called sulphocyanide.

is added and the solution stirred vigorously for a couple of minutes on the water-bath, filtered immediately and washed with hot acidulated water several times. The precipitate is treated in the funnel with a hot 10 per cent. solution of sodium hydroxide, giving sodium thiocyanate, which is obtained in a clean beaker, and cuprous hydroxide which is left on the paper. This is washed by hot water. The alkaline filtrate is acidified with dilute sulphuric acid and the free hydrothiocyanic acid is titrated (warm) by potassium permanganate, according to the reaction, $10HSCN + 12KMnO_4 + 8H_2SO_4 = 6K_2SO_4 + 12MnSO_4 + 10HCN + 8H_2O$.

The theoretical factor for changing the iron standard to the copper standard is 0.1892, but it is safer to standardize against copper on account of the slight solubility of the cuprous hydroxide in caustic alkali. The results so obtained agree with a factor of 0.1920. Of the metals likely to be present silver and possibly bismuth are the only ones which give insoluble thiocyanates under the conditions given. The silver would not interfere, for if not thrown out as chloride, the silver thiocyanate would be left with the cuprous hydroxide as it is not easily decomposed by alkali. The bismuth thiocyanate is soluble in acids and will usually be held in solution unless much is present. It is, however, precipitated as metallic bismuth if a large excess of sulphurous acid is used in effecting the reduction of the copper.

The weak point of the method is the precipitation of the cuprous thiocyanate, which requires careful regulation of the acidity, especially when bismuth is present. The advantages are the large quantity of permanganate used for small amounts of copper and the non-interference of arsenic and antimony.

The precipitation of copper as thiocyanate is used in alloys such as german silver, and to separate the bulk of the copper from the impurities in the analysis of pig copper.

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CHAPTER XII.

The Determination of Lead in Ores.

The well-known inaccuracy of the fire assay for lead has rendered more important the volumetric methods for its determination. The basis for the sale of ores is now, in many cases, the percentage actually present, as shown by wet methods, minus two per cent., instead of the fire assay results.*

The methods to be described are: First, the gravimetric, weighing as sulphate; second, the ferrocyanide; third, the molybdate. While there are many other excellent methods, notably Koenig's alkalimetric, and the various modifications of the chromate, the three described are sufficient.

Gravimetric as Lead Sulphate.

Treat from 0.5 to 1 gram of the very finely ground ore, depending on the amount of lead present, with 15–20 c.c. of concentrated nitric acid and a few drops of concentrated hydrochloric acid in a small covered casserole or Erlenmeyer flask; boiling until no further solution takes place and the sulphur (if the ore is a sulphide) is completely oxidized, adding more acids if necessary to complete the decomposition. Allow to cool slightly and add about 10 c.c. of sulphuric acid 1.41 sp. gr. (1 part concentrated acid to 1 of water) and evaporate to copious, dense fumes of sulphur trioxide. All the common ores of lead will be decomposed by this treatment, which is carried out as already described under copper. The addition of a little hydrochloric acid is not always required, but usually aids in the solution of the lead. The evaporation should be nearly to dryness so as to ensure the complete conversion of lead to sulphate and also to prevent there being present more than 1–2 per cent. of free sulphuric acid after dilution.

Allow the lead sulphate, etc., to cool and add cautiously about 100 c.c. of distilled water and boil for several minutes to dissolve the ferric sulphate, etc., allow to cool and add about 15 c.c. of

* See Iles, *School of Mines Quarterly*, 15, 336, 1894.

strong alcohol, stir well, allow to settle and decant through a small filter, leaving as much as possible of the insoluble sulphates and the silicious residue in the casserole or flask. Wash the residue by decantation thoroughly with water containing 1 per cent. sulphuric acid and 10 per cent. alcohol, pouring the washings through the filter, and wash finally with alcohol alone to remove the sulphuric acid. Place a clean beaker under the funnel, dissolve the lead sulphate from the residue in a strong hot solution of ammonium acetate, slightly acid with acetic acid; pour this solution through the filter into a clean beaker. Repeat this treatment until all the lead sulphate has dissolved; then wash the residue onto the filter and wash it finally with hot water. Most of the trouble in the determination of lead occurs just at this point; lead sulphate when free from other insoluble sulphates and freshly precipitated dissolves readily in hot ammoniun acetate, but when ignited or if contaminated by barium, strontium or calcium sulphates, boiling for half an hour with a liberal excess of ammonium acetate is absolutely necessary for its complete solution. The ammonium acetate is best made by neutralizing acetic acid with ammonia as the crystallized salt is an expensive reagent and has to be used in large quantities. On solution $Pb(C_2H_3O_2)_2$ and $(NH_4)_2Pb(SO_4)_2$ are formed.* The filtrate is acidified with dilute sulphuric acid, which reprecipitates the lead sulphate, alcohol is added as before (about 10 per cent.) and the precipitate filtered and washed, first with 1 per cent. sulphuric acid and 10 per cent. alcohol and finally with strong alcohol alone, either ethyl or methyl.

The ignition of the lead sulphate, when filtered on paper, gives considerable trouble and often inaccurate results because the carbon of the paper causes reduction to sulphide and sometimes to metallic lead, which requires reconversion, by nitric and sulphuric acids, to lead sulphate, often accompanied by mechanical loss. This difficulty can be overcome by using a Gooch crucible with asbestos alone, or as follows: Cut out two pieces of "acid-washed" filter paper so as to fit the bottom of the crucible accurately (using a 5-cent piece) and place them on the bottom of the crucible; then on top of these a thin layer of asbestos which has been washed

*On the solution of lead sulphate in ammonium acetate see also Noyes and Whitcomb, *Jour. Amer. Chem. Soc.*, 27, 747, 1905.

with dilute sulphuric acid, making a layer of about $\frac{3}{16}$ of an inch; then, while still wet, suck this down by a strong suction as tightly as possible and dry in an oven to constant weight at 110° C. After weighing moisten the filter and then pour in the solution containing the lead sulphate, using a very gentle suction at the beginning; wash as described, dry again at 110° C. and the increased weight is lead sulphate.

This method has been thoroughly tested and will yield results (when properly carried out) which are accurate to within a few hundredths of a per cent. When such accurate work is not required the alcohol may be omitted, but the use of the Gooch crucible is strongly recommended when the necessary suction can be obtained.

Lead sulphate is slightly soluble in water and quite soluble in concentrated sulphuric acid; it is almost insoluble in a 1 per cent. solution of sulphuric acid and insoluble in alcohol. Besides being soluble in ammonium acetate it is soluble in ammonium chloride and other ammonium salts. Boiling with alkali carbonates converts it to carbonate, which can then be readily dissolved in acids. Koenig dissolves the lead carbonate in standard nitric acid and then by titrating back with a standard solution of caustic soda using methyl-orange as an indicator, determines the quantity of acid required to dissolve the lead and so finds the lead present. This method has a great advantage over the other volumetric methods in the end point, which is sharp and satisfactory, while the others are spot tests and an allowance for the excess required must be subtracted, as in the zinc titration by potassium ferrocyanide. Lead sulphate is not volatilized if present when silica is driven off by hydrofluoric and sulphuric acids.*

In some cases it is preferable to precipitate the lead as sulphide and subsequently convert it to sulphate by strong nitric acid. It should be borne in mind that lead sulphide is the most soluble of the fifth- and sixth-group sulphides in hydrochloric acid, so that less than 2 c.c. of concentrated hydrochloric acid should be present in each 100 c.c. of solution. It can also be precipitated from a neutral or alkaline solution, or one slightly acid with nitric acid. This separation is often necessary with alloys containing antimony,

* Meade, *Jour. Amer. Chem. Soc.*, 19, 37, 1897.

tin, etc., where the sixth-group metal is subsequently removed by digesting with fixed alkali sulphide.

Ferrocyanide Method.

This method is the same as the gravimetric up to the point where the lead sulphate and insoluble residue have been washed free from sulphuric acid. Add to the residue in a flask or casserole at least 15 c.c. of a solution of commercial ammonium carbonate, saturated in the cold; heat to boiling, then allow to cool, and filter through the filter already used to retain any lead sulphate from washing the lead sulphate and residue. Wash the flask and precipitate till the washings show no alkaline reaction. Place in the flask 10 c.c. of 50 per cent. acetic acid and about 20 c.c. of water and boil till the lead carbonate has dissolved completely; dilute to nearly 100 c.c., warm to 60° C., and titrate by potassium ferrocyanide, using uranium nitrate as an indicator, as with zinc.

As in the zinc titration, uniformity in the conditions for titration are essential to correct results. The same standard solution can be used, or better, one half the strength, about 10 grams of crystallized potassium ferrocyanide per liter. With such a solution the allowance for the indicator should be about 0.8 c.c.; with the stronger solution, of course, it is less. This allowance is a matter of individual eyesight and should be determined on a blank test made up of 100 c.c. of water and 10 c.c. of 50 per cent. acetic acid at a temperature of 60° C.

The standard is obtained by treating portions of pure dry lead sulphate with ammonium carbonate, dissolving the lead carbonate in acetic acid and titrating under the conditions given.

The formula of the precipitate is nearly $Pb_2Fe(CN)_6$. It does not vary as greatly with changed conditions as the zinc ferrocyanide does, but as it is much more soluble equal care must be exercised in obtaining just the conditions given. The objectionable feature is the end point. Many other indicators have been tried, but nothing better than uranium salts has been found. The good feature of the method, which is, in fact, the reason for giving it a slight preference over all the others is that the impurities likely to be present are almost without effect. Antimony even if present to the extent of 0.200 gram is absolutely without effect. Bismuth

gives results slightly low, but as 0.360 gram only lowers the amount of 1 per cent. ferrocyanide used by 0.6 c.c. it will not affect results when present in small quantities. Calcium and strontium are without effect. Barium gives slightly low results. These statements are based on a series of experiments carried out exactly as the method is described here, the low results are not to be attributed to the titration but to the barium and bismuth interfering with the conversion of lead sulphate to carbonate, for this reason, in some cases, the amount of ammonium carbonate solution should be increased considerably, even up to 50 c.c., and also the time of heating.

The other metals which give insoluble ferrocyanides do not give insoluble sulphates or basic salts, so they pass into the filtrate when the lead sulphate and residue are filtered.

Molybdate Method.

This is based on the precipitation of lead as $PbMoO_4$ by a standard solution of ammonium molybdate in a hot solution slightly acid with acetic acid.* The end point is a spot test with tannin solution which turns yellow when the molybdate is in excess.

The standard ammonium molybdate is made by dissolving 9 grams of the pure salt in water and diluting to one liter; if the solution is not clear, add a few drops of ammonia. It is standardized by weighing out several portions of dry lead sulphate; dissolving them in hot ammonium acetate; adding 2–3 c.c. of acetic acid and titrating at about 90° C. till a drop of the clear solution gives a slight but distinct yellow color with a drop of a freshly prepared tannin solution, which contains about 1 gram to 300 c.c. of water. The most important point is to titrate hot. If the solution has become cool on account of slow work in titration, it should be heated again so that it is hot when the titration is finished. The solution should be decidedly acid with acetic acid. Here and also in the preceding method the plan given under zinc of dividing the solution roughly in half for titration can be utilized.

As an allowance must be made for the excess necessary to affect the indicator, uniformity in volume is essential; 200 c.c. is recommended. With this volume and the conditions given the

* H. H. Alexander, *Eng. and Min. Jour.*, April, 1893, p. 298.

allowance should not exceed 0.8 c.c. Many attempts have been made to obtain a more satisfactory end point for this method but so far in vain. The most satisfactory substitute has been devised by J. L. Danziger. Crystals of stannous chloride are dissolved in acetic acid till a saturated solution is formed; this is then saturated with ammonium thiocyanate. The solution so obtained gives a pink color with ammonium molybdate and is about as delicate as the tannin reaction.

To apply this method to an ore, follow the gravimetric method till the lead sulphate is dissolved in ammonium acetate, acidify with 2–3 c.c. of acetic acid, dilute to 200 c.c., heat to boiling and titrate as in standardizing.

Interferences. — Antimony and bismuth are without effect. Barium gives very low results; strontium low results; calcium very slightly low results, but not enough to affect ordinary work. As in the ferrocyanide method the action of these alkaline earth sulphates is to impede the solution of the lead, and the difficulty can be entirely overcome by thoroughly washing the lead sulphate and then boiling it repeatedly with sufficient ammonium acetate. For comparative results on these and other methods see Bull, *School of Mines Quarterly*, Vol. **23**, pp. 348–366, also *Zeits. für analytische Chemie*, Vol. **41**, pp. 653–674, 1902.

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CHAPTER XIII.

The Determination of Antimony in Ores.

On account of the great inaccuracy of the fire assay for antimony it has been abandoned and its place taken by a "wet assay." Before describing these methods a short description of the gravimetric determination will be given and a few of the more important separations of antimony.

The important ores of antimony are stibnite Sb_2S_3, cervantite Sb_2O_4, produced by the oxidation of the sulphide, and mixtures of the two usually containing more sulphide than oxide. As stibnite is soluble in hydrochloric acid containing a few drops of nitric, and cervantite is practically insoluble, we have three classes of ores; first, the soluble, stibnite and also the rarer oxide, senarmontite, Sb_2O_3; second, the insoluble; third, the partially soluble. They will be discussed in this order. The following method is taken largely from an article by Brown, *Jour. Amer. Chem. Soc.*, **21**, 780, 1899.

Gravimetric Method.

Soluble Ores. — One gram of the finely ground ore is placed in a small beaker, 25 c.c. of concentrated hydrochloric acid added, covered with a watch glass and boiled until the ore is apparently decomposed, which reduces the hydrochloric acid to about 15 c.c.; about 2 grams of tartaric acid are added and when dissolved 5 or 6 drops of concentrated nitric acid and the boiling continued for several minutes. The nitric acid causes a violent reaction, accompanied by a more complete decomposition of the ore. The solution is allowed to cool, diluted slightly, the residue filtered, and washed with water. The residue should be tested for antimony, unless the ore is known to be completely soluble. The filtrate is diluted to about 250 c.c. and the antimony is precipitated as sulphide by a stream of hydrogen sulphide, which is passed through for an hour. At the end the solution should be warmed to insure the conversion of any basic chloride (formed by the dilution) to sulphide; after standing for an hour to allow the precipitate to

collect and settle, it is filtered and washed with hydrogen sulphide water. There may be present in the ore, arsenic and also lead and other metals of the fifth group; the latter will be evident from the dark color of the sulphide. If the sulphide is impure, warm it with a strong solution of ammonium sulphide $(NH_4)_2S$, until the sulphides of arsenic and antimony have dissolved, then filter. The residue is lead sulphide, etc.; in it the lead can be found by methods already given. It should be remembered here that copper sulphide is slightly soluble in ammonium sulphide, so if it is present sodium or potassium sulphide should be used.

If mercury should be present and no copper use ammonium sulphide as mercuric sulphide is readily soluble in the fixed alkali sulphides. Tin is not likely to be present; it would dissolve with the arsenic and antimony readily if stannic sulphide, with difficulty if stannous sulphide. The separation of antimony from tin presents considerable difficulty. See the standard works on quantitative analysis and for the most recent descriptions of Clarke's method, etc. — Rossing, *Zeitschrift für analytische Chemie*, **41**, 1, 1902, and Henz, *Zeitschrift für anorganische Chemie*, **37**, 1–58, 1903.

The separation of the fifth and sixth groups is also incomplete by the ordinary methods when there are present mercury, copper and antimony, as sometimes happens with tetrahedrite (fahlerz). For this separation see Pretzfeld, *Jour. Amer. Chem. Soc.*, **25**, 198.

To the filtrate containing the arsenic and antimony as sulpho salts, dilute hydrochloric acid is added in slight excess, then the solution is diluted to ensure complete separation of the antimony sulphide, which is soluble in even moderately strong hydrochloric acid, and the mixture of sulphides of arsenic and antimony and sulphur is filtered on balanced filters, washed with cold water and dried at 110° C. for two hours or more to constant weight. This gives the total weight of the mixture. It is removed from the paper, ground up and mixed in a small glass mortar and an exact weight, of about 0.5 gram, is weighed off in a platinum or porcelain boat. This is placed in a piece of hard glass combustion tubing and the excess of sulphur, over that required to form Sb_2S_3 and the sulphide of arsenic, are driven off by heating in a current of carbon dioxide for 12–15 minutes. A steady stream of carbon

dioxide should be passed through the tube to displace the air before the heating is begun, so as to prevent oxidation; the heating should be gradual and the final temperature about 250° C., which is considerably below a dull red heat.

From the weight of the residue of black antimonous sulphide, the total antimony in the mixture of sulphides and sulphur is calculated and so the antimony in the ore. Should it be impossible to carry out this method, which is the best, the mixture of sulphide, or a portion of it, can be converted to oxide, Sb_2O_4, by treating repeatedly with strong nitric acid. This method is not recommended as it is almost always attended by mechanical loss, but if nothing better can be done, carry it out as follows: Transfer as much as possible of the dried precipitate to a porcelain crucible. Dissolve what adheres to the filter in freshly made ammonium sulphide, using as little as possible, and add the solution to the precipitate in the crucible; evaporate on a water-bath, add fuming nitric acid and allow to stand, carefully covered, for several hours; then add more nitric acid, evaporate again on a water-bath; next drive off the sulphuric acid formed and finally heat over a Bunsen burner (no blast), and weigh the Sb_2O_4. The arsenic will be volatilized.

Insoluble Ores. — One gram of the ore is mixed with 10 grams of flux, made up of equal parts of sodium carbonate and sulphur, in a porcelain crucible and covered by a layer of the same flux. The mixture is fused for about ten minutes, covered, in the muffle of an assay furnace or by a Bunsen burner. The heat should be low at first and gradually raised, but never high enough to volatilize antimony. The melt should be greenish; if it is yellow the decomposition is probably incomplete unless there is scarcely any iron present. The melt is treated with hot water and the sulphides of iron, lead, etc. (those which do not form soluble sulphosalts), filtered out. In the filtrate the antimony is precipitated as sulphide by hydrochloric acid and the precipitate treated as just described.

This is Rose's method of decomposition and it is also efficacious for the breaking up of cassiterite. Partially soluble ores can be treated as insoluble or treated first like soluble ores and the residue fused.

Properties of Antimony Sulphide. — Insoluble in water and dilute

acids; decomposed by concentrated nitric or sulphuric; soluble in concentrated hydrochloric; easily soluble in potassium or sodium hydroxide and alkali sulphides. Slightly soluble in ammonia and ammonium carbonate. The separation from arsenic by dissolving the sulphide of arsenic in ammonium carbonate is not quantitative. A better separation is Pattinson's. Obtain the arsenic and antimony in solution in the triad condition, add concentrated hydrochloric acid, so that the sp. gr. due to the acid shall exceed 1.17, and then precipitate the arsenic as sulphide. Arsenic sulphide is insoluble in concentrated hydrochloric acid, while in acid of 1.17 sp. gr. or over no antimony is precipitated.

Other methods of separating arsenic and antimony will be given under arsenic.

Volumetric Methods.

*Weller's Method.**

The ore is decomposed as already described and the antimony precipitated as sulphide, if arsenic is also present it must be separated. As tin does not interfere in this method Pattinson's separation can be used with stannous chloride to reduce the arsenic to arsenious chloride so that it will be promptly and completely separated as arsenious sulphide in the strong hydrochloric acid solution; then, after diluting the filtrate, the antimony is precipitated as sulphide, Sb_2S_3. Or the arsenic can be distilled off as arsenious chloride according to Fischer's distillation method (see next chapter).

The precipitated sulphide of antimony is dissolved in strong hydrochloric acid and is oxidized to the pentad condition by adding potassium or sodium chlorate in small portions and boiling till the excess of chlorine is expelled and the oxides of chlorine driven out. It is essential that the oxidation shall be complete and all excess of oxidizing agent expelled, as the method depends on measuring the iodine liberated by the pentad antimony; using a standard thiosulphate solution, as with copper.

After oxidation the solution is boiled down to very nearly 50 c.c.; this is ascertained with sufficient accuracy by making a mark on the beaker; then 20 c.c. of concentrated hydrochloric acid are added and the solution diluted to 200 c.c. with recently boiled

* Youtz, *School of Mines Quarterly*, July, 1903 (as modified by Falk).

cold water. Then 3 grams of potassium iodide dissolved in 10 c.c. of water are added, the mixture stirred thoroughly, and after waiting 3 minutes for the liberation of the iodine, the solution is diluted to 700 c.c. with cold water and titrated by sodium thiosulphate, using starch solution as indicator, till the blue color disappears. The end point is very sharp and satisfactory when these conditions are maintained exactly. It is very important that the amount of hydrochloric acid is kept constant; if too little is present basic iodides and chlorides of antimony separate out on dilution; if too much, the hydrochloric acid itself acts on the potassium iodide in the presence of air and liberates iodine. We obtain this constant quantity, no matter how much may be used in the solution of the sulphide, by boiling down to 50 c.c.; this will be acid of 20 per cent., the hydrochloric acid of constant boiling point. If it was weaker in the beginning, more water boils off, if stronger, more hydrochloric acid, until this strength of acid is reached. So by this means we obtain always the equivalent of 45 c.c. of concentrated hydrochloric acid.

The potassium iodide must be 3 grams, if more is used results which are too high are obtained. The liberation of iodine is not instantaneous so it is advisable to wait several minutes before titrating, otherwise the solution may be decolorized by the thiosulphate and then the blue color suddenly flashes back, because the reaction is not yet complete. When the end point is reached, under the right conditions, the decolorization lasts for several minutes.

The sodium thiosulphate solution used for the copper assay can be used here. The standard for antimony would be obtained as follows:

Copper standard : antimony standard :: atomic weight copper : one half atomic weight antimony.

It is more satisfactory to restandardize against antimony if absolutely pure metallic antimony can be obtained. Weigh out about 0.2 gram and dissolve this in about 50 c.c. or more of concentrated hydrochloric acid with 1–2 c.c. of concentrated nitric acid, then complete the oxidation by adding portions of 0.5 gram of potassium or sodium chlorate, boil out the oxides of chlorine and proceed as described. No tartaric acid is used in this method.

The reaction may be indicated as follows:

$$Sb_2O_5 + 4HI = Sb_2O_3 + 2I_2 + 2H_2O.$$

The antimony after oxidation is probably present as antimonic acid and after reduction by hydriodic acid it is present partly as antimonious iodide and partly as antimonious chloride, depending on the relative mass of hydriodic and hydrochloric acids. As tin in the stannic condition is not reduced by hydriodic acid, antimony can be determined in the presence of tin. This is of importance in the analysis of alloys.

This method is not free from theoretical difficulties, but it is very rapid and gives excellent practical results when the proper conditions are maintained. The same thiosulphate solution can be used as for copper and the end point is sharp.

Mohr's Method.

This is exactly the reverse of Weller's method. The reactions can be indicated as follows:

$$\underset{\text{Mohr}\rightarrow}{Sb_2O_3 + 2I_2 + 2H_2O} \rightleftharpoons \underset{\leftarrow\text{Weller}}{Sb_2O_5 + 4HI}.$$

In Mohr's method we prevent the reverse reaction by preventing any concentration of hydriodic acid by having an excess of alkali present. In order not to decompose the starch or absorb iodine this excess of alkali must be bicarbonate, so the exact reaction becomes

$$Na_3SbO_3 + I_2 + 2NaHCO_3 = Na_3SbO_4 + 2NaI + H_2O + 2CO_2.$$

The same statement and a similar reaction apply also to arsenic so it is evident that no arsenic can be present.

When the antimony is in the pentad condition it must be reduced by heating with sulphurous acid. To the acid solution add 30 c.c. of sulphurous acid (about 5 per cent. SO_2) and boil till most of the sulphur dioxide is expelled, then add a second portion of 30 c.c. and boil out the sulphur dioxide completely, then add about two grams of tartaric acid, to prevent the subsequent precipitation of antimony as hydrated oxide and make the solution alkaline with sodium bicarbonate, add about 20 c.c. of a saturated solution in

excess, cool and titrate with N/10 iodine, using starch as indicator, at a volume of about 200 c.c.

When the antimony is separated as sulphide, either Sb_2S_3 or Sb_2S_5, it is washed from the filter paper with a small quantity of water and then dissolved in hydrochloric acid. This, by the liberation of hydrogen sulphide, reduces the antimony to antimonious chloride, so that after adding tartaric acid and neutralizing the excess of acid by alkali, and then adding an excess of sodium bicarbonate it is ready for titration.

It is advisable to run a blank made by neutralizing the same amount of hydrochloric acid in the same way and adding the same excess of sodium bicarbonate, in order to see whether a small quantity of iodine is required when there is no antimony present. If this amounts to more than 0.1 c.c. it should be subtracted.

This method can be used for arsenic in exactly the same way, omitting the tartaric acid.

Conclusion. — Formerly antimony was weighed as sulphide, after washing with alcohol, to remove the water, then with carbon bisulphide to take out the free sulphur and drying at 250° C. Unless the sulphides of arsenic are removed as described above, the results are always high and the method is only to be used for very small quantities, under 1 per cent. A comparison of results has shown the weighing as oxide to be slightly low and that the Mohr and Weller methods give accurate results.

The application of the volumetric methods to insoluble ores containing both arsenic and antimony will be indicated in the next chapter.

CHAPTER XIV.

The Determination of Arsenic in Ores.

Distillation Method.

This method consists in distilling off the arsenic as arsenious chloride, and so affords a most perfect separation from antimony and tin. Although it requires considerable apparatus, it must be regarded as the standard method of separation; besides being applicable to ores it is even better for material containing only very low percentages of arsenic — pig copper, etc. It was devised by Professor Emil Fischer, of Berlin.

Arsenic ores are almost always sulphides. They may be decomposed by the fusion methods given under antimony, and the arsenic precipitated as sulphide. The original ore, or the sixth-group sulphides, is treated as follows: Place about two grams of potassium chlorate on the bottom of a beaker; on this place the weighed sample of ore, from 0.5 to 3 grams, depending on the richness, or the precipitated sulphides; then about a gram more of potassium or sodium chlorate, sufficient to cover the ore; pour in cautiously little by little a mixture of 30 c.c. of concentrated hydrochloric acid and 10 c.c. of water, cover the beaker and heat on a water-bath till the decomposition is complete and the oxides of chlorine, etc., driven off so as not to use up the ferrous salt added later. It is very important that the oxidation is complete to H_3AsO_4, as the arsenious chloride would be lost by boiling. If antimony is also to be determined, filter off any residue on asbestos, transfer the solution to a distilling flask (about 400 c.c.) using concentrated hydrochloric acid to rinse out the beaker, etc., add 5 to 20 grams of ferrous sulphate, depending on the quantity of arsenic present and make the solution up to about 200 c.c. in volume with concentrated hydrochloric acid. Connect the flask with a short condenser and under the end place an Erlenmeyer flask, about 250 c.c. containing a little water so as to cover the end of the condenser tube. Heat the flask on an asbestos pad by a burner; the arsenic acid is promptly reduced by the large excess of ferrous salt and

forms arsenious chloride; this with hydrochloric acid begins to distill over before a temperature of 100° C. is reached. They are condensed and collect in the Erlenmeyer flask. If this becomes very hot it should be surrounded by ice water. The apparatus should be set up in a place free from draughts so as to avoid back pressure. The distillation is continued until about half the original volume remains. Remove the Erlenmeyer flask and then the burner, when cool add another 100 c.c. of concentrated hydrochloric acid and repeat the distillation, catching the distillate as before. This is continued till no more arsenic distills over, which can easily be ascertained by testing a portion of the last distillate with hydrogen sulphide. Unless there is a very large quantity of arsenic present two or at most three distillations are all that are required. The solution in the flask must not be allowed to become too small or in other words the boiling point must not be allowed to rise above 107° C. for the temperature of the vapor and 112° C. for the solution; above this point antimony will begin to distill over. The distillation can be hastened by connecting the distilling flask with a second flask containing concentrated hydrochloric acid, this is heated so that a stream of hydrochloric acid gas passes in constantly, so that the strength of the acid is maintained and the removal of the arsenious chloride facilitated (like distilling with steam).

When the separation is complete, the apparatus is allowed to cool and the antimony from the distilling flask is precipitated by hydrogen sulphide after diluting largely and the antimony sulphide treated as already described. The arsenic is all in the distillate in the arsenious condition; it can be determined by nearly neutralizing the large excess of acid by soda, then adding a strong solution of sodium bicarbonate and titrating by $N/10$ iodine, exactly as given under antimony.

If a gravimetric method is to be used the arsenic is precipitated by hydrogen sulphide after diluting somewhat. Under these conditions the arsenic precipitates immediately as arsenious sulphide with very little sulphur, as it is entirely in the triad condition. If the amount is small it can be filtered on a Gooch crucible, washed with alcohol then with carbon bisulphide and after drying at 110° C. weighed as sulphide. The results are slightly high. If

the amount of arsenic is considerable, over 20 per cent., the error will increase proportionally and the arsenic must be dissolved, oxidized and finally weighed as magnesium pyroarsenate. The sulphide is dissolved in fuming nitric acid, the excess of acid and oxides of nitrogen removed by boiling (for manipulation compare antimony sulphide when paper is used); or dissolve from the Gooch crucible by ammonia, evaporate down on a water-bath and then oxidize, or dissolve through by a small quantity of sodium hydroxide and oxidize by boiling with bromine.

Precipitation of Magnesium Ammonium Arsenate.

The conditions for the precipitation of magnesium ammonium arsenate are similar to those for magnesium ammonium phosphate, but as the precipitate is more soluble and also more easily decomposed on ignition greater care must be used. When the arsenic is all in the pentad condition neutralize the acid solution with ammonia and add a slight excess. The volume should not exceed 100 c.c.; add magnesia mixture slowly, drop by drop, till in considerable excess, then alcohol equal to one third the volume of the solution and allow to stand in the cold over night. Filter on asbestos in a Gooch crucible and wash with 2.5 per cent. ammonia containing alcohol, then with alcohol alone, dry and ignite very gently to constant weight; weigh the $Mg_2As_2O_7$.

Separations of Arsenic and Antimony.

The action of hydrogen sulphide on arsenic and antimony is important but confusing.

The following separations are used:

Bunsen's Method. — When hydrogen sulphide is passed into an acid solution containing pentad arsenic and pentad antimony at the room temperature and then the hydrogen sulphide driven out by a current of air, antimonic sulphide, Sb_2S_5, only is precipitated. The hydrogen sulphide reduces the arsenic slowly, and if the excess is promptly driven out when the precipitation is complete, a satisfactory separation is effected.

Pattinson's Method. — In the separation described under antimony the hydrochloric acid was so strong that no antimony sulphide could form; here to get a prompt precipitation of arsenic it

should be reduced before passing in hydrogen sulphide. When stannous chloride is used care must be taken to avoid an excess, which would precipitate metallic arsenic.

Neher's Method. — The solution containing arsenic and antimony, completely oxidized, and at least two volumes of concentrated hydrochloric acid to one of solution (*i. e.*, 1.14 sp. gr.), is cooled to zero and saturated by a rapid stream of hydrogen sulphide. The arsenic is completely precipitated as pentasulphide, As_2S_5. McCay obtains the same result by saturating the solution containing pentad arsenic in the cold with hydrogen sulphide and then heating in a closed bottle (under pressure) in a water-bath. The arsenic can be filtered on a Gooch crucible and weighed as pentasulphide, As_2S_5.

These separations are in accord with the theory that in a hot solution hydrogen sulphide reduces the arsenic first and then precipitates it as As_2S_3 mixed with sulphur; at the ordinary temperature this reduction goes on slowly, at zero it is not perceptible. Also as the acid increases the amount of pentasulphide increases, the limit being Neher's method where at 0°C. and in a strongly acid solution the precipitation is entirely as As_2S_5. So under ordinary conditions we obtain various mixtures of As_2S_5, As_2S_3 and sulphur, depending on the temperature and the acidity.

For information on the formation of sulphoxy acids of arsenic, which by breaking up give these sulphides, see McCay, *Jour. Amer. Chem. Soc.*, **24**, 661, 1902. And for more information on the separation, see Treadwell's "Quantitative Analysis," pp. 150–154 (German edition). When arsenic is to be removed in the course of analysis with the fifth and sixth groups, it should be reduced by sulphurous acid and the excess expelled. This is accomplished readily under pressure by heating in a strong bottle in boiling water, wrapped up in a towel to prevent flying glass, in case of an explosion.

Volumetric Methods.

The most important determination of arsenic for mining engineers is in ores, where it is present in amount not over 10 per cent. and for this determination some modification of Pearce's method is usually employed. The method is not free from objections and gives low results on arsenopyrite. This method and one recently

devised by Danziger and Buckout * which is also applicable to arsenopyrite will be described.

PEARCE'S METHOD AS MODIFIED BY BENNET † is based on the following facts. Arsenic when fused with a mixture of potassium nitrate and sodium carbonate is completely oxidized and forms sodium arsenate, Na_3AsO_4, which is soluble in water, while antimony forms a quite insoluble sodium metantimoniate which is left behind when the melt is leached with water, together with oxide of iron, insoluble carbonates, etc. The filtrate contains (beside Na_3AsO_4) Na_2SO_4, Na_2SiO_3, $Na_2Al_2O_4$ and an excess of Na_2CO_3; this is acidified and the carbon dioxide expelled; then neutralized exactly and the arsenic precipitated as silver arsenate, Ag_3AsO_4, by an aqueous solution of silver nitrate. It is this neutralization which has given trouble; in the original method it was effected by ammonia, but as the precipitate (Ag_3AsO_4) is readily soluble either in nitric acid or ammonia, it was essential to obtain exactly the neutral point. The second plan for neutralizing was proposed by Canby, the addition of a cream of zinc oxide; this method will give a sufficiently neutral solution if the zinc oxide is allowed to remain in contact with the solution over night. The latest suggestion is that of Bennet to use acetic acid and a sensitive indicator like phenolphthalein.

The precipitate of silver arsenate is filtered off and the silver in it determined by Volhard's thiocyanate titration using ferric alum as an indicator. The method is therefore an indirect titration of the arsenic, and for three atoms of silver found there must have been present from the ore, one atom of arsenic. So the arsenic value for the thiocyanate solution is obtained from the silver standard by using the proportion, — atomic weight silver to one third atomic weight arsenic.

Solutions Required. — Aqueous nitrate of silver, made by dissolving silver nitrate crystals in water. (The nitric acid solution used to test for chlorides will not do here.)

A ten per cent. solution of ferric sulphate or a saturated solution of iron ammonium alum as indicator.

A solution of ammonium thiocyanate containing about 8 grams

* *School of Mines Quarterly*, April, 1903.

† *Jour. Amer. Chem. Soc.*, 21, 431, 1899.

per liter. This is standardized by dissolving portions of pure silver, about 0.2 gram each in nitric acid, 1.16 sp. gr., diluting to about 100 c.c., adding 5 c.c. of the indicator and titrating until a faint permanent reddish color is produced. The silver is precipitated as thiocyanate. The end point is the production of red ferric thiocyanate.

Both the silver and the arsenic standards should be placed on the bottle as the solution may be used for the determination of silver in alloys, etc. This solution keeps well and therefore does not require frequent restandardizing.

Flux. — Make up a sufficient quantity of flux containing two parts of potassium nitrate by weight, to one part of sodium carbonate.

Assay. — Place a layer of the flux on the bottom of a Russia iron crucible, mix the weighed portion of the ore, 0.25 to 1 gram, depending on the quantity of arsenic, with 8–10 times its weight of the flux and place this on top of the first layer; cover this with a layer of potassium nitrate. Porcelain crucibles may be used, but they usually break, owing to the contraction of the flux on cooling.

Heat the crucible very gently and gradually, holding the burner in the hand and allowing the flame to heat different parts of the crucible in turn. The heating requires attention or arsenic will be lost with a high-grade ore. There must be no odor or fumes of arsenic at this point. After the fusion has become quiet, the heating is continued for several minutes and the contents caused to rotate to ensure complete fusion and oxidation. Allow to cool and leach with hot water, filter and wash the residue very thoroughly with hot water; acidify with nitric acid and boil vigorously till all the carbon dioxide is expelled. If any precipitate, such as hydrated silica, forms here it may be filtered out, as it would interfere with the filtration of the silver arsenate, but not with the accuracy of the results. Allow the solution to cool completely; add a few drops of phenolphthalein and then dilute sodium hydroxide solution (not ammonia or sodium carbonate on account of the indicator) till the solution turns pink, then acetic acid drop by drop till the color is discharged, stirring after each addition, so as to stop when there is but a drop of acetic acid in excess. Then, to the cold solution add a slight ex-

cess of aqueous silver nitrate, filter the brick-red silver arsenate and wash it with cold water till free from silver. As silver acetate is sparingly soluble, this must be completely washed out as well as the excess of nitrate. Dissolve the precipitate through the paper with dilute nitric acid into a clean beaker; dilute to about 100 c.c.; add 5 c.c. of the ferric indicator, and titrate as in standardizing.

Sodium Peroxide Method.

Sodium peroxide has been found to be an admirable reagent for the decomposition of arsenic ores; its action is the same as the mixture of potassium nitrate and sodium carbonate to form sodium arsenate, but it acts more rapidly and effectively in preventing loss by volatilization with high-grade ores. After boiling to destroy the excess of peroxide and filtering off the residue, we have an alkaline solution containing sodium arsenate. There are at least three volumetric methods by which the arsenic can be determined.

(1) Indirectly as silver arsenate as just described.

(2) By standard alkali. Acidify the alkaline solution with hydrochloric or nitric acid in slight excess, boil out carbon dioxide, then add methyl-orange and titrate till the solution turns yellow, with a dilute solution of sodium hydroxide. This marks the neutralization of the excess of hydrochloric or nitric acid and of one hydrogen of the arsenic acid; we have now in solution NaH_2AsO_4; add a few drops of phenolphthalein, and titrate to a pink color with a standard solution of sodium hydroxide. The amount of alkali used is that required to neutralize the second hydrogen. Hence for each molecule of sodium hydroxide used there is present one atom of arsenic. This method is only outlined as it is not as accurate as the others.

(3) Measuring the arsenic present by the amount of iodine liberated, as in Weller's method for antimony. This gives accurate results when carried out as follows: Fuse one gram of ore with 15 grams of sodium peroxide in a small iron crucible, allow to cool, add water carefully, then boil to expel hydrogen peroxide, allow to cool, wash into a 250 c.c. flask and fill to one c.c. above the mark and mix thoroughly. Filter through a small double filter paper (dry) discarding the first 10 c.c. of filtrate if cloudy. Transfer 100 c c. of the clear filtrate to a beaker, acidify with con-

centrated hydrochloric acid, boil to expel carbon dioxide, add 110 c.c. of concentrated hydrochloric acid and allow to cool.* To the cold solution add 3 grams of potassium iodide dissolved in 10 c.c. of water, stir and allow to stand for five minutes, then dilute with 500 c.c. of cold water containing 5 c.c. of concentrated hydrochloric acid and titrate with sodium thiosulphate solution, stirring well and adding the starch solution as usual when the solution has become light yellow.

The method as described is very rapid and does away with the slow filtration and subsequent washing of the precipitate with sodium carbonate solution. The ferric oxide from the melt can not be dissolved and reprecipitated, as the ferric hydroxide carries down some arsenic.

Note. — The ore and peroxide should fill the crucible not over one third full, with a layer of peroxide on top. Heat slowly at first until the mass is fused, then increase to a strong red heat and rotate the contents of the crucible (holding it by tongs in the flame) to facilitate complete decomposition of the ore.

The results, using the standard calculated from iodine or potassium dichromate, are apt to be about 1 per cent. low, so that it is better to standardize against freshly resublimed arsenious oxide, As_2O_3, as follows: Weigh out portions of 0.2–0.25 gram of resublimed arsenious oxide into small beakers; add to each about 0.5 gram of potassium chlorate and about 20 c.c. of concentrated hydrochloric acid and boil till the oxidation of the arsenic is complete and all yellow color has disappeared from the solution; add water and concentrated hydrochloric acid so that the final bulk is 100–150 c.c. and consists of half concentrated hydrochloric acid and half water (20 per cent. actual HCl). Cool, add 3 grams of potassium iodide and titrate as in the ore. Calculate the arsenic standard from the number of c.c. used. This is another titration where the results are varied by changes in the conditions of titration; here the important points are the temperature, the acidity, the amount of potassium iodide and the time allowed for the liberation of the iodine. When uniform conditions are maintained in standardizing and in titrating the results are very exact.

* If salts separate out, decant and dissolve in the least amount of water necessary; combine the two solutions.

It only remains to indicate a procedure for ores containing both arsenic and antimony. Decompose the ore with sodium peroxide, as given, leach, boil, filter and precipitate the antimony by Bunsen's method (page 119), filter out the antimonic sulphide and titrate the arsenic in the filtrate as just described. To obtain the antimony dissolve the residue from the fusion in hydrochloric acid, filter, precipitate the antimony in the filtrate by hydrogen sulphide; add this to the sulphide already obtained: dissolve and titrate by either of the methods given under antimony ore.

ADDITIONAL REFERENCES TO BOTH ARSENIC AND ANTIMONY.

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CHAPTER XV.

Slag Analysis.

Under the title of Slag Analysis, nearly the whole subject of analytical chemistry and assaying might be discussed, for a great majority of the elements, both common and rare, are to be found in slags. No such attempt will be made here; what follows is merely a description of the technical analysis of some of the most important types of slags. For a more detailed and complete discussion of the subject the reader is referred to an article by Dr. Joüet on the Analysis of Slags and Cinders, in the *School of Mines Quarterly*, Vol. **22,** Nos. 1 and 2.

If the sample of slag has been chilled suddenly, it can usually be decomposed by acids, if allowed to cool slowly, a fusion with mixed carbonates is required. The important points to be shown in a technical analysis are: The ratio of bases to silica, the ratio of R_2O_3 bases to those of the RO type, the quantity of valuable metal present in a slag, from copper smelting, copper, etc.

For convenience in treating this subject the following classification is made.

Iron Slags. — The slags from the blast furnace in the production of pig iron, though containing much less iron than those which follow. They contain roughly 40–50 per cent. silica, 15–20 per cent. alumina, etc., 30–40 per cent. lime, magnesia, etc., besides iron, manganese, alkalies, sulphur, phosphorus, etc. The slags from basic processes are often rich in phosphoric acid. For this determination see Wiley's Agricultural Analysis, Vol. II.

Manganese Slags. — The slags formed in the production of spiegel, lower in silica than the iron slags, but containing up to ten per cent. of manganese. The difficult points in their analysis are the decomposition and the separation of manganese from alumina.

Lead Slags. — Containing roughly silica 32 per cent., iron 28 per cent., lime, etc., 20 per cent., the remainder being lead, zinc, antimony, sulphur, etc.

Copper Slags. — Similar in composition to the lead slags, but

usually without lead or zinc and containing about half a per cent. of copper.

These four groups of slags fall naturally into two divisions, the iron and manganese slags and the lead and copper slags.

A general scheme will be given for each of these divisions, followed by a few comments and special precautions and by some separate methods for the determination of particular constituents. The methods will not be given in detail as they have already been discussed in these notes.

Iron and Manganese Slags.

In this scheme (page 128) provision has been made for titanium, barium, zinc, nickel and cobalt and also for the removal of the higher groups, although they are not usually present. When these are omitted the analysis becomes quite similar to that of limestone. Phosphorus and sulphur must be determined in separate portions: See Iron Ore.

In manganese slags, the fusion with mixed carbonates will usually be required to get complete decomposition, using a liberal quantity of flux and a long fusion. In making the basic acetate separation, the excess of acetic acid must be very small in order to get complete precipitation of alumina and must be repeated to remove the manganese which is sure to come down under these conditions.

The determinations of greatest importance and in many cases all that are required, are silica, oxides of iron and aluminum, lime and magnesia. When the slag is soluble and only approximate results are required the determinations can be made as follows:*

Portion for Silica and Oxides of Iron and Aluminum. — Weigh out half a gram of the sample, place this in a casserole, add about 20 c.c. of water and stir well, then 15–20 c.c. of strong hydrochloric acid, heat to boiling, while stirring to break up any lumps; then evaporate rapidly to dryness and bake, take up with hydrochloric acid and water, boil and filter, ignite and weigh the silica (impure). In the filtrate the alumina is precipitated, together with ferric hydroxide, by ammonia and ammonium chloride. This should be reprecipitated, to free it from lime and magnesia, then ignited and weighed as usual.

* See also Lord's "Notes on Metallurgical Analysis," p. 201 et seq.

General Scheme for Iron and Manganese Slags.

Dissolve 1 gram in HCl and a few drops of HNO_3 or fuse with $NaKCO_3$ and a little KNO_3 and then dissolve in HCl. Evaporate to dryness, after adding a few drops of H_2SO_4; dehydrate silica; take up with dilute HCl; boil; filter.

Residue.

SiO_2, TiO_2, $BaSO_4$; weigh: expel SiO_2 by HF and H_2SO_4; reweigh: fuse residue with Na_2CO_3; dissolve in HCl; dilute, filter out the $BaSO_4$ and add filtrate to main filtrate. From the weight of $BaSO_4$ the barium can be calculated.

Filtrate.

Saturate with H_2S, to remove 5th and 6th groups, including Pt from crucible; filter.

Precipitate.

Sulphides usually rejected. May be used for As, Sb, etc., if present.

Filtrate.

Oxidize the iron by HNO_3 or H_2O_2; neutralize with Na_2CO_3; add $NaC_2H_3O_2$ dilute and boil (basic acetate precipitation), filter and repeat the precipitation.

Precipitate.

Redissolve again in HCl and precipitate by ammonia. Ignite and weigh the Fe_2O_3, Al_2O_3, TiO_2 and P_2O_5.

Fuse with $KHSO_4$, dissolve, reduce and titrate the iron: calculate to Fe_2O_3 and obtain the Al_2O_3 by difference. The percentage of Al_2O_3 can be subsequently corrected for P_2O_5 and TiO_2 if present.

Filtrates.

Combine the filtrates from the two basic acetate precipitations and evaporate; if any $Al(OH)_3$ separates, add it to the ammonia precipitate. Add bromine and heat; filter.

Precipitate.

MnO_4xH_2O Dissolve and determine Mn as $Mn_2P_2O_7$ or by Volhard's method.

Filtrate.

Make the solution alkaline with ammonia and saturate with H_2S.

Precipitate.

ZnS, NiS, CoS. Treat with HCl 1.02 sp. gr. saturated with H_2S.

Residue.

NiS, CoS dissolve in aqua regia, evap. to fumes with H_2SO_4 and determine electrolytically.

Solution.

$ZnCl_2$ Precipitate as $ZnNH_4PO_4$ or titrate by $K_4Fe(CN)_6$.

Filtrate.

Precipitate the calcium as oxalate.

Precipitate.

CaC_2O_4 weigh as CaO or as $CaSO_4$ or dissolve and titrate the $H_2C_2O_4$ by $KMnO_4$.

Filtrate.

Precipitate the Mg as $MgNH_4PO_4$, ignite and weigh as $Mg_2P_2O_7$.

Portion for Lime and Alumina. — Treat a gram as above, using more water and acid; evaporate to dryness and heat to dehydrate the silica; add hydrochloric acid and water, boil, pour into a 500-c.c. flask, rinse out the casserole with more hydrochloric acid and water, adding this also to the flask; dilute to about 300 c.c., add ammonia in slight excess, dilute to the mark (500 c.c.), mix thoroughly; filter through a dry paper and determine lime and magnesia in an aliquot part (250 or 200 c.c.) by the usual methods.

Lime may be precipitated as oxalate in the filtrate from silica without removing iron and alumina; the filtrate is heated to boiling and a slight excess of ammonia is added, then an oxalic acid solution, more than enough to combine with the lime, then ammonia is added again and finally enough oxalic acid to redissolve any iron. The solution is heated to boiling and the calcium oxalate filtered and either weighed or titrated as usual. The object here is to get sufficient oxalic acid to prevent the precipitation of iron. The method is not accurate and is spoiled by the presence of manganese.

None of these short methods is applicable to manganese slags.

Lead and Copper Slags.

If silver is present it will be largely with the first residue of silica, lead sulphate, etc. In this case it should be leached with ammonia before removing the lead sulphate.

In the scheme given on page 130 the barium is likely to be low, as the barium sulphate is somewhat soluble in ammonium acetate and also on account of the final reprecipitation in the presence of hydrochloric and tartaric acids. When barium is absent and the antimony in the residue disregarded this portion of the analysis becomes very simple.

Similarly in the main filtrate, if the trace of lead which escapes precipitation as sulphate is disregarded and bismuth is absent the fifth-group sulphides may be dissolved and the copper titrated at once.

It is not advisable to employ the volumetric method for antimony here as the amount is small and difficult to dissolve from the sulphur thrown down with it.

In treating the filtrate for iron, ammonia may be used instead

General Scheme for Lead and Copper Slags.

Treat 1 gram of the finely ground slag in a casserole with water, concentrated hydrochloric acid and a few drops of nitric acid or else fuse and dissolve in hydrochloric acid; add sulphuric acid and evaporate to fumes, dilute and filter, wash well to remove calcium sulphate.

<table>
<tr><td colspan="3">Residue.
SiO_2, $PbSO_4$, possibly $BaSO_4$ and Sb_2O_3, leach out the lead sulphate by hot ammonium acetate, using as little as possible; filter.</td><td colspan="3">Filtrate.
Add about 1 c.c. of conc. HCl and saturate with H_2S.</td></tr>
<tr><td colspan="2">Residue.
SiO_2, $BaSO_4$, Sb_2O_3; weigh: drive off the SiO_2 by HF and H_2SO_4; reweigh and determine silica by loss.
$BaSO_4$ and Sb_2O_4 remain; fuse with Na_2CO_3; take up with HCl and $H_2C_4H_4O_6$; filter.</td><td rowspan="2">Filtrate.
Precipitate the lead as $PbSO_4$, filter and weigh.
In the filtrate precipitate any antimony as sulphide and add this to the main ppt. of 5th and 6th group metals.</td><td colspan="2">Precipitate.
CuS, Sb_2S_3, traces of PbS and possibly Bi_2S_3, digest hot with Na_2S solution.</td><td rowspan="2">Filtrate.
Oxidize the iron. Precipitate iron and alumina as basic acetates, and proceed from this point according to the scheme given for iron and manganese slags.</td></tr>
<tr><td>Precipitate.
$BaSO_4$, weigh.</td><td>Filtrate.
Precipitate the antimony by H_2S and add to main precipitate.</td><td>Residue.
CuS, PbS (traces), Bi_2S_3(?).
Dissolve in HNO_3; evaporate to fumes to throw out lead as sulphate.
Filtrate; separate the bismuth and then determine the copper either electrolytically or volumetrically.</td><td>Solution.
Na_3SbS_3 etc. acidify, filter out the Sb_2S_3+S; weigh as Sb_2S_3 or as Sb_2O_4.</td></tr>
</table>

of the basic acetate if manganese is absent. The percentage of iron is usually high and no particular difficulties are likely to be met.

Sulphur is occasionally determined in lead slags. This is either done by the Fahlberg-Iles method * or as follows: † One gram of the slag is treated in a casserole with a few c.c. of water, 10 c.c. of concentrated nitric acid and finally 20–25 c.c. of concentrated hydrochloric acid; boiled for about 10 minutes, more hydrochloric acid added, and then evaporated to dryness and baked on a hot plate. When cold it is taken up with concentrated hydrochloric acid and water and boiled thoroughly; then the free acid neutralized with ammonia and exactly 6 c.c. of concentrated hydrochloric acid added and the boiling and stirring continued till it is certain that all the iron oxide and lead sulphate are in solution; diluted to 200 c.c., 25 c.c. of 10 per cent. barium chloride added and the solution boiled for 15 to 20 minutes, filtered and washed. The precipitate is ignited in a platinum crucible, the silica driven off by hydrochloric and sulphuric acids and the barium sulphate weighed. If the slag is not chilled, it will not be decomposed thoroughly, so the barium sulphate will be impure. With soluble slags this method gives good results and is much shorter than the Fahlberg-Iles.

When the results are required in a very short time accuracy must give way to rapidity. So time is saved by working at once on a number of separate portions. (See Furman's "Manual on Assaying.")

The following methods are employed for these slags:

Silica. — Dissolve half a gram in water and hydrochloric acid, filter, ignite and weigh the silica (which is of course impure).

Barium. — Dissolve half a gram in hydrochloric acid, add sulphuric acid and evaporate to fumes, neutralize the excess of sulphuric acid by ammonia, add 6 c.c. of hydrochloric acid, dilute to 200 c.c., boil and filter, weigh the silica and barium sulphate.

Iron. — One gram is dissolved and the iron titrated by either the dichromate or the permanganate method.

* Iles, Decomposition and Analysis of Slag, *School of Mines Quarterly*, **5**, p. 357.

† Miller and Thompson, paper read at N. Y. Section Amer. Chem. Soc., December 4, 1903.

Manganese. — One gram, using Volhard's method.

Zinc. — One gram by the ferrocyanide method.

Copper. — One gram or more by the colorimetric method.

Lead. — One gram or more by volumetric methods or a larger portion by fire assay.

Silver is usually determined by fire assay.

The other determinations have been indicated under the iron and manganese slags.

When ferrous iron is to be determined, Cooke's method, as given by Hillebrand, Bulletin 305, U. S. Geological Survey, is to be used.

Objection can easily be made to these schemes; they are incomplete on one hand and too long for some purposes on the other; but they are given as representing as much as is likely to be required of the mining engineer and as affording plans which can be amplified, modified or shortened to meet special needs. If more complete schemes are desired, they are to be found in the article by Dr. Joüet already mentioned. As rocks and slags have much in common from an analytical standpoint, Dr. Hillebrand's bulletin on rock analysis will give much valuable information.

CHAPTER XVI.

Flue Gas Analysis.

Any engineer is almost sure to have charge of some kind of a power plant, usually one where the heat of combustion of coal is the source of power; in order to ascertain the efficiency at which the plant is run, he must know at least the analysis, better also, the calorific power, of the coal, and the composition of the flue gas and the ash — the results of combustion.

The examination of the ash is for unburned carbon and requires no additional description.* The determinations required in the flue gas are carbon dioxide, carbon monoxide, oxygen and nitrogen; the first two are of the greatest importance, as the higher the carbon dioxide and the lower the monoxide, the more efficient is the combustion. If this is obtained by the introduction of an excessive quantity of air, both the carbon dioxide and monoxide will be low.

All that is required of the engineer is a knowledge of how to determine these four important constituents, really only three for the nitrogen is determined by difference, in order to ascertain whether the fuel is being used economically. This is obtained more satisfactorily by a number of analyses at frequent intervals, each made with rapidity, than by one analysis made with all the precautions and corrections, on account of the variations in the composition of the gas due to additions of fresh fuel, changing of draughts, etc. Therefore no mention will be made here of the so-called "exact" gas analysis, where all the measurements are made over mercury and allowance made for changes in temperature, barometer, etc., except to refer the reader to Hempel's Gas Analysis, recently translated by Professor Dennis. We need only consider the most simple application of "technical" gas analysis.

Gas analysis is a branch of volumetric analysis and the results are always expressed in percentage by volume. Now, as the variation of volume of all gases for temperature and pressure is the

* See coal analysis.

same, the percentage by volume at any given temperature and pressure will be the same as under the standard conditions, 0° C. and 760 mm. It is therefore only when some particular constituent is absorbed and afterwards determined gravimetrically or by titration, that it is necessary in the "technical" analysis to apply the corrections for temperature, pressure and tension of aqueous vapor. However, variations of temperature or of pressure must be most carefully guarded against while the analysis is in progress, as these would vitiate the results. Whenever possible, the analysis is conducted in a room of even temperature, preferably with a northern exposure. All measurements are made at the atmospheric pressure and over water which has been previously saturated with a gas similar to that under examination.

If the temperature remains constant the tension of aqueous vapor is also constant, and when the analysis is conducted rapidly the variations of the atmospheric pressure are not likely to affect the results seriously. So as these conditions are practically constant, the results expressed in percentage by volume will agree within an allowable error of say 0.1 per cent. of the results calculated to the standard conditions. Unless there is a sudden barometric change or by carelessness the gas becomes changed in temperature, the error is likely to be less than the inaccuracy in reading the volumes.

Saturating the water over which the gas is measured or kept, and also the reagents, with the gases present, which are not to be absorbed by this particular reagent, deserves special emphasis. All gases are soluble in water to some extent and as carbon dioxide is soluble to the extent of about one volume of the gas to one volume of water, the error due to this cause may be great. The saturation is easily accomplished by running through one or two analyses of the gas, after the apparatus has been filled with water, reagents, etc., before making the analysis, the results of which are to be used.

The Orsat apparatus is the most convenient for flue gas analysis, as it is compact and portable.* It is assumed in these notes that this form of apparatus is to be used.

* A description of this apparatus can be found in the text-books given at the end of this chapter or in the circulars of the dealers in chemical apparatus.

Reagents.

Carbon dioxide is removed by a strong solution of potassium hydroxide, 500 grams of commercial caustic potash to a liter of water: each cubic centimeter of this reagent absorbs about 40 c.c. of carbon dioxide. This is the first reagent used with the flue gas.

Oxygen is absorbed by an alkaline pyrogallate solution, made by dissolving (as far as possible out of contact with the air) 5 grams of pyrogallol, $C_6H_3(OH)_3$, in 100 c.c. of the potassium hydroxide given above. Pyrogallol or, as it is frequently termed, pyrogallic acid, is a triatomic phenol, when dissolved in potassium hydroxide the three hydrogens of the hydroxyl groups are replaced by potassium atoms. When oxygen is absorbed no definite reaction takes place, but acetic acid, and brown humus-like substances are formed. The reagent will be quickly exhausted if exposed to the air; each c.c. absorbs readily about 2 c.c. of oxygen after which the absorption becomes very slow. This is the second reagent used in the flue gas analysis; it is evident that as it contains an enormous excess of caustic alkali it would, if used first, absorb carbon dioxide as well as oxygen.

Carbon monoxide is absorbed by a hydrochloric acid solution of cuprous chloride, which is made as follows: * Cover the bottom of a large wide-mouthed bottle with black oxide of copper, not necessarily pure, to a depth of about half an inch; fill nearly full with hydrochloric acid 1.1 sp. gr.; add about a hundred pieces of stout copper wire, cut in lengths of about six inches, so that they shall reach from the bottom to the top of the bottle; allow to stand, shaking occasionally, till the solution is colorless; then withdraw for use. The action is that the cupric oxide dissolves in the hydrochloric acid giving cupric chloride, this in turn dissolves copper from the wires forming cuprous chloride, the reagent desired.

The wires keep up the strength of the solution and reduce any cupric chloride formed by the air back to cuprous; the solution should be nearly colorless when used. The amount of carbon monoxide absorbed per c.c. is given variously by different authorities, but it is safe to assume that it will absorb an equal volume

* Gill, "Gas Analysis for Engineers," p. 34.

of carbon monoxide. The reaction is supposed to result in the formation of an unstable addition product, $Cu_2Cl_2.CO$. As there are usually only a few tenths of a per cent. of carbon monoxide in flue gas, this reagent will last for some time if protected from oxidation or if kept in contact with metallic copper. This is the third and last reagent used with flue gas.

SAMPLING.

The sample should be taken as close as possible to the point where the flame ends and at the place in the flue of smallest cross-section, to prevent admixture of air and to get a sample of the gas which is really the result of the combustion in progress when the sample is obtained. Tubes are usually inserted in the wall of the chimney or other flue, which should penetrate to the center and contain asbestos to filter out dust, etc. They may be made of hard glass (combustion tubing), porcelain or metal depending on the temperature. Iron tubes are, however, objectionable as they become coated with oxide, which is reduced by the carbon monoxide in the gas with an increase in the amount of carbon dioxide.

The end of the tube is provided with a cork or rubber stopper through which passes a smaller glass tube, which is connected by a short rubber tube with the sample tube. Many convenient forms of apparatus for samples of gas can be had from the dealers, but all that is necessary is a large pipette, 200–250 c.c., provided with a short piece of rubber tubing at both ends and two clamps.

As the draught of the chimney must be overcome in taking the sample, some form of aspirator is needed. Water pumps are convenient when water pressure is at hand, but a simple and serviceable pump * can be made by reversing the valve of an ordinary large-sized bicycle pump.

The aspirator is attached to the sample tube and the flue gases drawn through for several minutes to displace the air which fills the tube and connections; then the ends of the sample tube are closed (by the clamps on the rubber tubes) and the sample is taken to the Orsat apparatus.

* Devised by Irving Langmuir.

Analysis.

The Orsat apparatus consists essentially of three pipettes containing the reagents already described and a measuring tube graduated from 0 to 100 c.c. in tenths, provided with a levelling bottle, so that the pressure of the gas can be made equal to that of the atmosphere. The measuring tube and connections are filled with water by turning a stop-cock and raising the levelling bottle; then the tube containing the sample is connected by one end, while the other is placed under water, to prevent admixture of air when the sample of gas is removed; the connections are opened and by lowering the levelling bottle a little more than 100 c.c. of the flue gas is drawn into the measuring tube; the sample tube is then closed and disconnected and the excess of flue gas above 100 c.c. driven out by raising the levelling bottle so that the liquid in the measuring tube and in the bottle shall coincide with the 100-c.c. mark. Then the stop-cock is turned to prevent the escape of gas and the analysis is begun. The gas is run into the first pipette, containing potassium hydroxide. By raising the levelling bottle, the gas displaces the alkali solution, which passes into the rear portion of the pipette, displacing in turn air which expands a rubber bag. In this way the reagents are kept from contact with the atmosphere. In the pipettes are a number of glass rods; when the reagent is displaced these rods remain wet and so give a large surface for the absorption of carbon dioxide from the flue gas. After three minutes the gas is drawn back into the measuring tube, care being taken that the reagent comes back to exactly the point at which it stood before on the capillary tube connecting with the pipette; and the gas is remeasured at the atmospheric pressure. The decrease in volume gives the percentage of carbon dioxide. In order to ensure the complete absorption of any constituent it is well to run the gas over again into the pipette for three minutes and then back and take a second reading; if more than two treatments are required, the reagent is becoming exhausted and should be renewed. When the carbon dioxide has been completely removed, the gas is run into the second pipette, containing alkaline pyrogallate, and the oxygen removed in the same way. As this reagent is likely to become appreciably weakened in a very short time, a third or fourth treatment is often

necessary. After the oxygen has been removed and the second decrease in volume noted, the gas is run over into the third pipette containing cuprous chloride, for the removal of carbon monoxide; then back and the final reading taken. The residual gas is considered nitrogen.

Great care should be taken when making the readings to have the level in the levelling bottle and the measuring tube the same, so that the gas is under exactly atmospheric pressure each time.

Results.

While it is not the province of analytical chemistry to discuss the results, it is to be expected that the carbon dioxide will be from 5–12 per cent., the carbon monoxide 0.0–0.4 per cent., the oxygen together with the carbon dioxide should usually be between 20 and 21 per cent., and the remainder nitrogen.

While there is some variation in the percentage of oxygen in the air in different places, country and city, streets and parks, it is very slight, and 20.9 per cent. is very close to the correct percentage. Now if we burn carbon in air completely to carbon dioxide, as the volume of carbon dioxide is equal to the volume of oxygen used, according to Avogadro's law, the sum of the percentages of oxygen and carbon dioxide should equal that of the oxygen in the air, *i. e.*, 20.9 per cent. But it often happens in the analysis of flue gas that the sum of these two does not equal 20.9 per cent.; for if any carbon monoxide is produced we get two volumes of carbon monoxide for each volume of oxygen, hence the percentage of nitrogen is diminished; on the other hand if hydrocarbons such as methane, etc., are present, from bituminous coal, we get one volume of carbon dioxide from two volumes of oxygen, as the water condenses, and therefore an increase in the percentage of nitrogen over that in the air. (See also Calculations of Analytical Chemistry, Chapter VIII.)

For further information on flue gas analysis the reader is referred to Gills' "Gas and Fuel Analysis for Engineers," Stillman's "Engineering Chemistry," and Blair's "Chemical Analysis of Iron." For a complete discussion of gas analysis see Hempel's "Gas Analysis," translated by Dennis, and Winkler's "Technical Gas Analysis," translated and enlarged by Lunge.

CHAPTER XVII.

References to Additional Analyses.

The last chapter concluded the descriptions of the analyses required of the mining engineers at Columbia University, but not all those frequently needed in practice; so this final chapter will contain references to descriptions of a number of additional analyses which are often required of mining engineers, metallurgists or chemists.

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